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CARBURETING AND COMBUSTION

IN

ALCOHOL ENGINES

BY

ERNEST SOREL

TRANSLATED FROM THE FRENCH

BY

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AND

JOHN PRESTON

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CHAPTER I.

TRANSLATOR'S INTRODUCTION.

THE recent action of the United States Congress, by which the use of alcohol for industrial purposes is permitted without the payment of the internal revenue tax levied upon the alcohol in spirituous liquors, has developed a wide-spread interest in the possible uses to which alcohol may now be put. The internal revenue tax of two dollars and twenty cents per gallon on 100 per cent alcohol — a tax which has been maintained at this figure for many years — has prevented the extensive use of alcohol in the various arts and industries for which its properties naturally fit it.

As a fuel any extensive use was prohibited by the high cost, due to the internal revenue tax. While the cost of manufacture of a gallon of strong alcohol has probably not much exceeded thirty cents, until the recent congressional action the market price has been about two dollars and fifty cents. Under the new law alcohol, which has been properly denatured by the addition of a definite proportion of poisonous and repulsive ingredients to render it unfit for drinking, is exempt from the payment of any internal revenue tax and hence may be sold at the cost of manufacture.

The physical properties of alcohol are such as to make it an admirable fuel in many ways; but it differs sufficiently from the other familiar liquid fuels so that special forms of apparatus are necessary for its use. So little has been done in this country in experimenting upon suitable apparatus that we naturally look for information to the continental European countries, where during the last ten years the use of denatured alcohol has been rapidly expanding.

Many tests of alcohol engines have been made in both Germany and France, but the most extensive study of the subject which has yet been printed is the work, recently published in France, a translation of which is here presented. The original researches of which this book is largely an account were made under a commission from the French minister of agriculture. The book deals but slightly, and then only in a general way, with what might be called the structural details of the alcohol engine. As a matter of fact the only important essential difference between an alcohol engine and an internal combustion engine for using any other fuel, lies in the apparatus for properly preparing and proportioning the explosive mixture composed of the vaporized fuel and air.

This work takes up and treats exhaustively the physical and chemical principles upon which the design of all satisfactory alcohol engines must depend. Most of the data herein given had never been investigated before M. Sorel began his researches. A thorough comprehension of the results of these researches will serve to prevent many useless and expensive experiments in inventing alcohol engines; and, in fact, it does not seem too much to say, that an adequate understanding of these results will prove indispensable to the design of a satisfactory alcohol engine.

Explanation of terms used. — The extensive use of internal combustion engines is still so recent that no univer-

sally accepted system of nomenclature is in use, and it may tend toward ease in understanding the work to explain here some of the terms and methods used in translating.

The word *carbureter* is used for the mechanism which converts the liquid alcohol into vapor and mixes it with air; and the process of so preparing the explosive mixture is called *carbureting*. When alcohol is used as an engine fuel, it is a common practice abroad to mix with it some hydrocarbon having a higher heat of combustion per pound than has alcohol. Such a mixture of fuels is mentioned many times in the book and, after much hesitation, has been called *carburated* alcohol for lack of a better term.

Gasoline has been uniformly used to represent any light petroleum distillate, while *benzene* has been used to represent the substance whose chemical symbol is C_6H_6, whether in the pure or commercial state. While largely similar to gasoline in its properties, this substance is relatively more abundant abroad on account of its occurrence as a gas house by-product.

Whenever the strength of alcohol is mentioned as a per cent, the proportion of alcohol by volume, in the mixture with water or other ingredients, is signified unless the per cent by weight is expressly stated. This is in accordance with the customary usage in the United States, and is the method followed in France. To avoid confusion, it is well to know, however, that in Germany the universal practice is to state the strength of alcohol by giving the amount present as a per cent by weight.

In general, the French text has been closely followed in the translation. In a few places a slight condensation has been adopted.

Since most of the numerical data refer to chemical and physical laws in connection with which the metric units

are in common use in this country, the metric units are retained throughout. Probably the greatest objection to this usage is in connection with temperature values. On this account in some places temperatures are given in their Fahrenheit equivalents as well as in their Centigrade values.

As the reader may desire to compare some of the numerical results with data from other sources expressed in English units, the following conversion factors are given which may be easily applied, and which will suffice to transform most of the numerical quantities given in the book:

1 kilogram = 1000 grams = 2.205 pounds.

1 meter = 100 centimeters = 1000 millimeters = 39.37 inches = 3.281 feet.

1 cubic meter = 35.31 cubic feet.

1 liter = 1.057 quarts = .2642 gallon = .03531 cubic foot.

1 Centigrade temperature degree = $\frac{9}{5}$ Fahrenheit degrees.

To change a temperature in Centigrade degrees to a Fahrenheit temperature, let F be the Fahrenheit temperature and C be the Centigrade temperature. Then,

$F = \frac{9}{5} C + 32.$

1 calory = 3.968 British thermal units.

1 calory per kilogram = $\frac{9}{5}$ British thermal units per pound.

1 calory per cubic meter = .1124 British thermal units per cubic foot.

1 metric horsepower = 75 kilogram meters per second = .9863 British horsepower.

A fuel consumption of 1 kilogram per metric horsepower per hour = 2.235 pounds per British horsepower per hour.

Recent American tests of alcohol as an engine fuel.— During 1906 the United States Department of Agriculture conducted a series of experiments in the mechanical engineering laboratories of Columbia University with alcohol as a fuel in various types of internal combustion engines in extensive use throughout the United States.

The object of these experiments was: to determine what difficulties would be encountered in using alcohol as a fuel for the types of engines already in general use; to ascertain whether the engines could be made to operate satisfactorily on alcohol fuel, and what the consumption of alcohol would be as compared with the fuels for which the engines were originally designed; and finally, to throw light upon the action of alcohol as an engine fuel so that some information might be obtained as to the nature and extent of the modifications necessary in the engine mechanisms, in order that the most economical consumption of alcohol fuel might be obtained.

The following engines were used in these tests:

A 15-horsepower, 2-cylinder, vertical, 4-cycle Nash gasoline engine.

A 6-horsepower, horizontal, 4-cycle, International Harvester Co. gasoline engine.

A 6-horsepower, horizontal, 4-cycle, Weber gasoline engine.

A 6-horsepower, vertical, 4-cycle, Fairbanks, Morse & Co. gasoline engine.

A 6-horsepower, horizontal, 2-cycle, Mietz & Weiss kerosene engine.

A 40-horsepower, 4-cylinder, American Mercedes automobile gasoline engine.

A 40-horsepower, 4-cylinder, Pope-Toledo automobile gasoline engine.

A 2-horsepower, vertical, 2-cycle Mianus marine gasoline engine.

All the above engines were operated successfully on commercial 94 per cent grain alcohol. The changes necessary in the adjustments of the fuel supplying mechanism were in most cases simple and easily made, although a large amount of experimentation was necessary to determine the best arrangements and adjustments in order to secure the most economical fuel consumption.

The results obtained will be briefly summarized for each of the engines.

The Nash engine had a spray carbureter. The air supply after passing the spray orifice entered a mixing chamber through a fuel mixture valve. An auxiliary air valve admitted fresh air from the outside directly to the mixing chamber, and between the mixing chamber and the engine was the regular cam operated admission valve. The amount of air passing the spray orifice and hence the suction operating on this orifice, was controlled by the setting of the auxiliary air valve. The greater the opening of this auxiliary valve the larger the proportion of air entering the mixing chamber directly, and the smaller the amount which passed the spray orifice, and hence also the smaller the amount of fuel which entered the fuel mixture.

The hit-and-miss governor acted by preventing the fuel mixture valve between the spray orifice and the mixing chamber from opening. But on a miss stroke the regular admission and exhaust valves were operated by the cams as usual. Hence, on a miss stroke the engine cylinder receives a supply of fresh air which has entered the mixing chamber through the auxiliary air valve. The pure air on a miss stroke scavenges the cylinder of the products of combustion remaining from the previous explosion. If the auxiliary air valve is not much open its throttling action on a miss stroke produces a vacuum in the cylinder on the

suction stroke sufficient to reduce materially the weight of the air charge drawn into the cylinder. In such a case an indicator diagram shows for a miss stroke a compression line distinctly lower than the usual compression line.

The engine was started with alcohol in the fuel chamber by injecting a few drops of gasoline into the air suction. After the first explosion was obtained the engine would run perfectly on the alcohol, provided the fuel and air valves were properly set. It was found that the opening of the fuel admission valve needed to be nearly twice as large for alcohol as for gasoline in order to secure a sufficient supply of the fuel. The operation of the engine on the alcohol fuel was regular, smooth, and noiseless. As compared with gasoline the rate of propagation of combustion with the alcohol seemed to be smaller, and it appeared less explosive. This is shown by the reproductions of indicator cards shown in Plate I. Cards 1 and 2 were obtained with ignition taking place when the piston was 13 per cent of its stroke before reaching the dead centre. Cards 3 and 4 were taken with the ignition 3 per cent before dead center. Nos. 1 and 3 are gasoline cards, and 2 and 4 alcohol cards. The former show the more rapid combustion with the resulting production of large waves on the cards.

Card No. 5, Plate I, is a gasoline card showing the large cycle produced on the first explosion after a miss during which the cylinder had been cleared of burned gases by the charge of pure air which entered the cylinder during the miss stroke. When this card was taken, a considerable excess of gasoline fuel was being supplied to the engine. This excess was sufficient to make the fuel mixture for the ordinary explosions rather slow burning as shown by the indicator cards, but with the increased amount of

air present in the cylinder after the miss, the excess of fuel became useful, increasing the charge of available combustible mixture and forming a highly explosive mixture.

Card No. 6, Plate I, shows the effect of introducing a considerable excess of alcohol fuel. Apparently the alcohol was not entirely vaporized as fast as supplied, but some of the alcohol supplied collected in the mixing chamber or in the engine cylinder in the liquid state. When the fuel valve remained closed on a miss stroke, the fresh air admitted vaporized the liquid alcohol remaining from the previous fuel admissions. Thus was formed a feebly combustible mixture which gave an explosion on what would ordinarily be a miss stroke. That this explosion took place when the fuel admission valve remained closed is shown on the indicator card by the lowered compression line. The fact was also verified by careful observation of the engine while running.

The ordinary compression on the Nash engine was about 70 pounds per square inch. After the comparative consumptions of alcohol and gasoline were obtained, plates were attached to the inner faces of the cylinder heads, raising the compression to nearly 90 pounds. The engine was again run on both alcohol and gasoline, although with the latter fuel it was difficult to make a satisfactory test on account of the tendency to pre-ignition, producing objectionable hammering. Next still thicker plates were put on the cylinder heads raising the compression to 110 pounds, and the alcohol consumption determined. With the lowest compression the best fuel consumptions obtained were 0.72 pound with gasoline, and 1.17 pounds with alcohol per brake horsepower hour. For the intermediate compressions the best consumptions were, respectively, 0.71 and 1.12 pounds. For the highest compression the

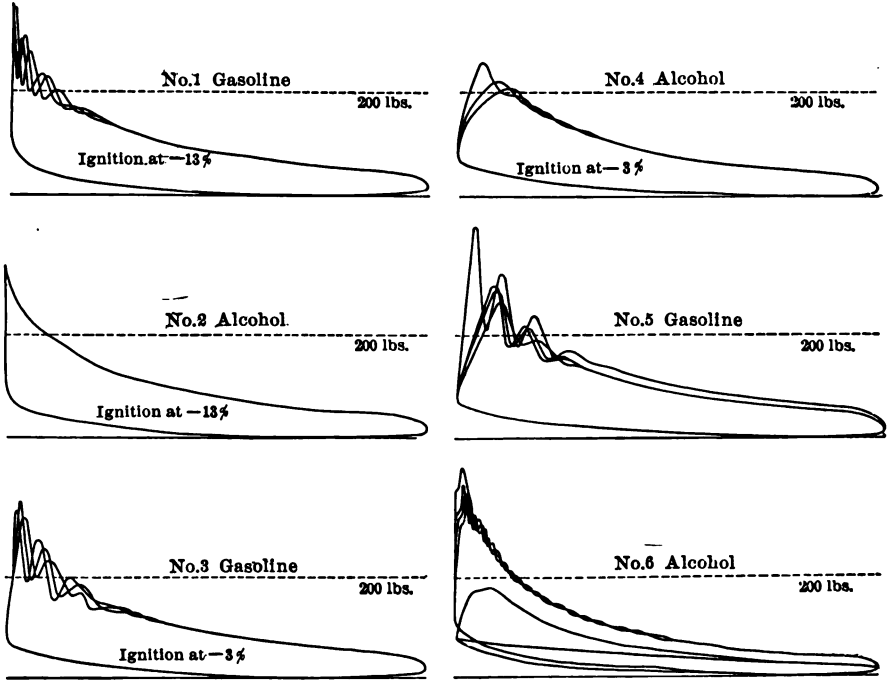


PLATE I. REPRESENTATIVE INDICATOR CARDS FROM THE NASH ENGINE.

best alcohol consumption obtained was 1.12 pounds per brake horsepower hour.

With the highest compression using alcohol and with the ignition set very early, maximum pressures of over 400 pounds were shown by the indicator without there being any perceptible knocking or hammering.

During the tests it was observed that the maximum power obtainable from the engine when using alcohol fuel was plainly greater than when gasoline was used.

At the most economical fuel consumptions the mean effective pressure as shown by the indicator cards, with both gasoline and alcohol, was between 80 and 85 pounds per square inch, but the mean effective pressure could be raised to 90 pounds by using a considerable excess of fuel.

The International Harvester Co. engine. — This engine had a hit-and-miss governor and used a spray carbureter. Its initial compression was about 73 pounds per square inch. Many tests were made on this engine with both alcohol and gasoline as fuel to determine the effect upon fuel consumption of change in the brake load and in the fuel needle valve setting.

This engine could be started as easily in the laboratory on alcohol as on gasoline when the proper adjustments had been determined. The maximum horsepower obtainable with alcohol was greater than with gasoline, and in every way the running of the engine was as smooth and satisfactory on alcohol as on gasoline.

It was found that the fuel consumption depended largely upon the setting of the needle valve, and for any given load was approximately proportional to the needle valve opening. The best consumption was obtained with the smallest needle valve setting under which the engine could carry the load. The consumption of fuel could be increased to nearly double the minimum by opening the

needle valve, before the excess of fuel would prevent the engine from carrying the load. At all settings between the two extremes the operation of the engine was perfectly satisfactory so far as external appearances would indicate, and the excessive consumption of fuel could be determined only by measurement. Plate II, based upon the results of these tests, shows the consumption of alcohol and gasoline for different loads and needle valve settings. The fuel consumption per brake horsepower hour naturally increases as the brake load is diminished. With the extreme mixtures the fuel is slow burning in the engine cylinder and the consumption is improved by using a very early ignition.

Plate III shows representative indicator cards taken during different tests with gasoline fuel, and Plate IV cards with alcohol fuel. When all these cards were taken the load on the engine was approximately five horsepower. Each card is marked with the needle valve setting used during the test, the mean effective pressure determined from the average of all the cards taken during each test, and the fuel consumption in pounds per brake horsepower hour. The time of ignition was the same for all these cards except Nos. 1 and 7, Plate IV, which were taken with a much earlier ignition than the other cards.

The cards show that the highest rate of propagation of combustion and the highest mean effective pressure correspond to a fuel consumption much in excess of the lowest possible.

The best consumptions obtained with this engine were 0.69 pound of gasoline or 1.23 pounds of alcohol per brake horsepower hour. The mean effective pressure at best consumption was about 90 pounds per square inch for either fuel, and considerably higher values were obtained with an excess of fuel.

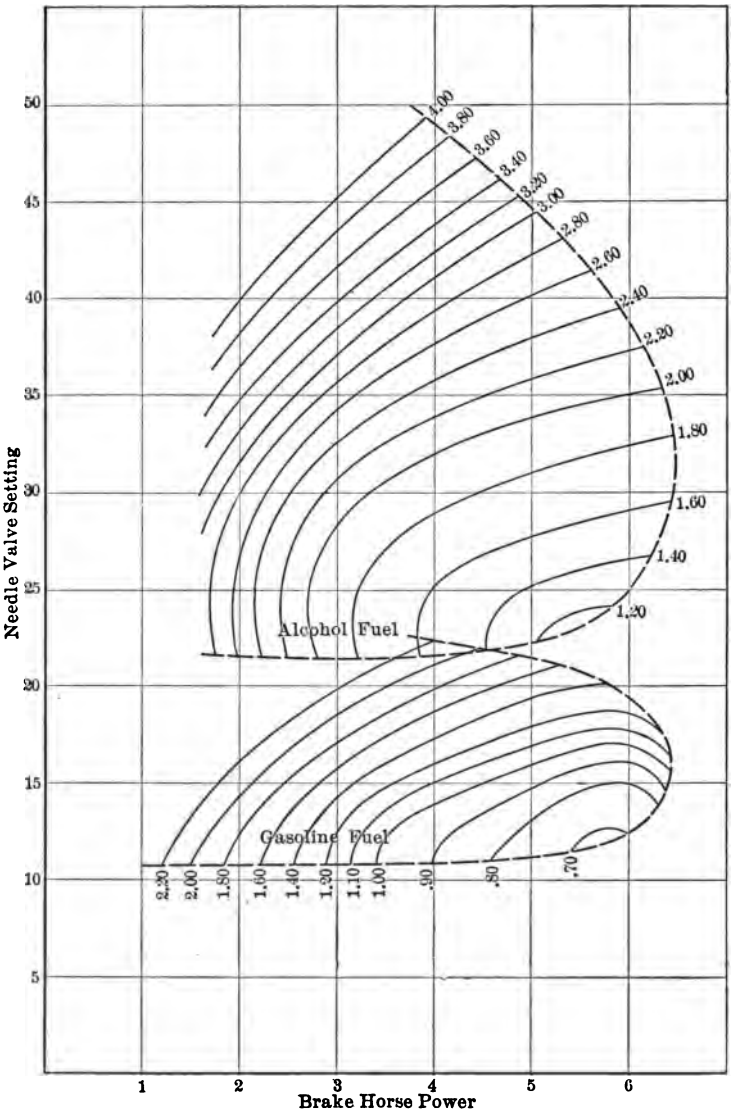


PLATE II. DIAGRAM SHOWING FOR THE INTERNATIONAL HARVESTER CO. ENGINE, THE RELATIVE CONSUMPTION OF ALCOHOL AND GASOLINE IN POUNDS PER BRAKE HORSE POWER HOUR, FOR VARIOUS BRAKE HORSE POWERS AND NEEDLE VALVE SETTINGS.

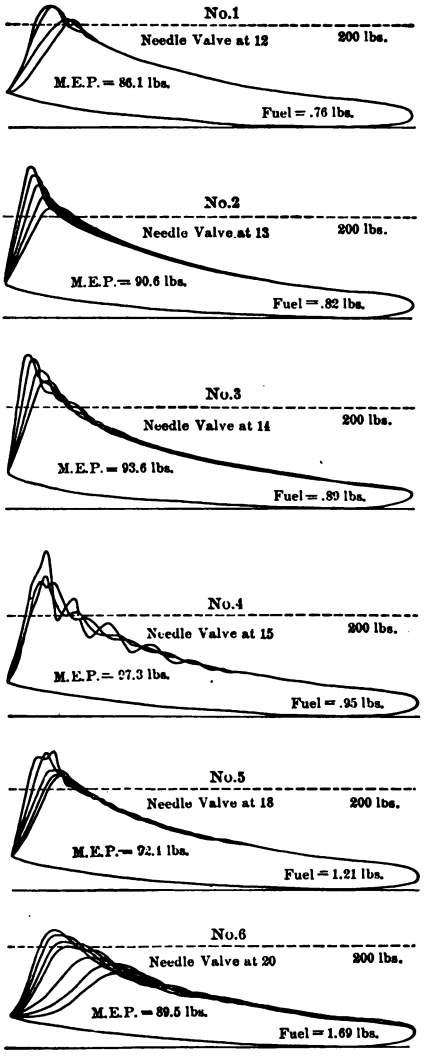


PLATE III. REPRESENTATIVE INDICATOR CARDS OBTAINED WHEN USING GASOLINE AS FUEL.

With a small load on the engine and a large excess of alcohol fuel supplied, very curious effects were observed. On the first fuel admission after a miss no explosion would occur. On the next fuel admission an explosion would occur, producing a mean effective pressure of 126 pounds per square inch as shown by the indicator card. The odor of alcohol could be perceived in the exhaust at the end of a long exhaust pipe, and the exhaust gases could be ignited.

The Weber engine. — This engine is similar to the last engine mentioned, and tests showed the same general variations of fuel consumption with changes in needle valve settings and brake loads. Successive explosions varied greatly in the maximum and average pressures produced. With alcohol fuel slow speeds gave a better consumption than high speeds. Plate V shows this engine fitted up for testing with friction brake, fuel measuring device, and indicator attached. The other engines were tested in a similar manner.

Fairbanks, Morse & Co. engine. — This was a throttle governed engine with the compression raised to 128 pounds per square inch. As before it was found that the fuel consumption for any given load depended chiefly upon the settings of the air and fuel admission valves. This engine had a spray carbureter, and the effect of heating the air supply before it entered the carbureter was tried. No improvement in fuel consumption was obtained with the heated air. It was found that when the air was heated to about 125° F. the charge would self-ignite and the engine would run steadily and satisfactorily under full load with the battery current cut off. When the temperature of the entering air was raised to 150° F., self-ignition took place so early as to reduce materially the maximum load which the engine could carry. Still there was no hammering or

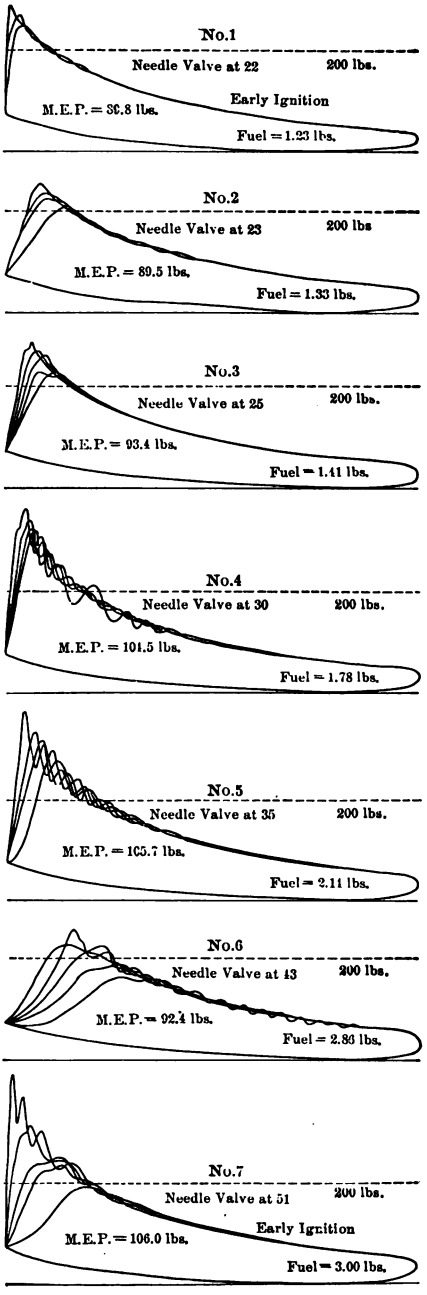


PLATE IV. REPRESENTATIVE INDICATOR CARDS OBTAINED WHEN USING ALCOHOL AS FUEL.

knocking in the engine cylinder. The best fuel consumption obtained with alcohol was 1.13 pounds per brake horsepower hour.

Mietz & Weiss kerosene engine.— This hot bulb engine was made to run satisfactorily on alcohol fuel by increasing the size of the fuel injection orifice and increasing the amount of the fuel pump stroke. The maximum power obtained from the engine on alcohol was greater than could be obtained with kerosene. The best consumption obtained with kerosene was 0.98 pound, and with alcohol 1.60 pounds per brake horsepower hour.

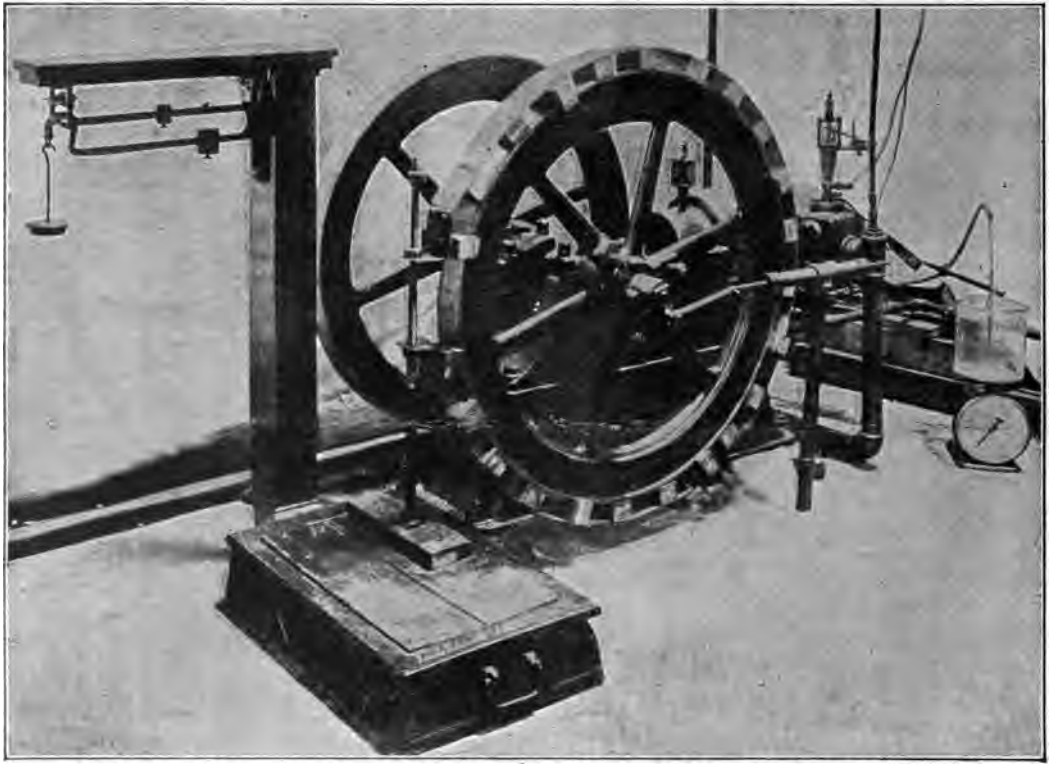
American Mercedes, Pope-Toledo, and Mianus engines. — These high-speed engines were all run successfully and satisfactorily on alcohol fuel. The consumption of alcohol bore in general about the same ratio to the consumption of gasoline for each engine as had been obtained in the other engines.

The following general conclusions are drawn as a result of the investigations conducted by the United States Department of Agriculture:

1. Any gasoline engine of the ordinary types can be run on alcohol fuel without any material change in the construction of the engine. The only difficulties likely to be encountered are in starting and in supplying a sufficient quantity of fuel, a quantity which must be considerably greater than the quantity of gasoline required.

2. When an engine is run on alcohol its operation is more noiseless than when run on gasoline, its maximum power is usually materially higher than it is on gasoline, and there is no danger of any injurious hammering with alcohol such as may occur with gasoline.

3. For automobile air-cooled engines alcohol seems to be especially adapted as a fuel, since the temperature of the engine cylinder may rise much higher before auto-ignition



17 PLATE V. WEBER ENGINE AS FITTED UP FOR TESTING WITH ALCOHOL AS FUEL.

takes place than is possible with gasoline fuel; and if auto-ignition of the alcohol fuel does occur no injurious hammering can result.

4. The consumption of fuel in pounds per brake horsepower, whether the fuel is gasoline or alcohol, depends chiefly upon the horsepower at which the engine is being run and upon the setting of the fuel supply valve. It is easily possible for the fuel consumption per horsepower hour to be increased to double the best value, either by running the engine on a load below its full power or by a poor setting of the fuel supply valve.

5. These investigations also showed that the fuel consumption was affected by the time of ignition, by the speed, and by the initial compression of the fuel charge. No tests were made to determine the maximum possible change in fuel consumption that could be produced by changing the time of ignition, but when near the best fuel consumption it was shown to be important to have an early ignition. So far as tested, the alcohol fuel consumption was better at low than at high speeds. So far as investigated, increasing the initial compression from 70 to 125 pounds produced only a very slight improvement in the consumption of alcohol.

6. It is probable that for any given engine the fuel consumption is also affected by the quantity and temperature of cooling water used, and the nature of the cooling system by the type of ignition apparatus, by the quantity and quality of lubricating oil, by the temperature and humidity of the atmosphere, and by the temperature of the fuel.

7. It seems probable that all well-constructed engines of the same size will have approximately the same fuel consumption when working under the most advantageous conditions.

8. With any good small stationary engine as small a fuel consumption as .70 pound of gasoline, or 1.16 pounds of alcohol per brake horsepower hour may reasonably be expected under favorable conditions. These values correspond to .118 and .170 gallon, respectively, or .95 pint of gasoline and 1.36 pints of alcohol. Based on the high calorific values of 21,120 British thermal units per pound of gasoline, and 11,880 per pound of alcohol, these consumptions represent thermal efficiencies of 17.2 per cent for gasoline and 18.5 per cent for alcohol.

But calculated on the basis of the low calorific values of 19,660 British thermal units per pound for gasoline and 10,620 for alcohol, the thermal efficiencies become 18.5 for the former fuel and 20.7 for alcohol. The ratio of the high calorific values used above is, gasoline to alcohol, 1.78. The corresponding ratio of the low calorific values is 1.85. The ratio of the consumptions mentioned above is, alcohol to gasoline, 1.66 by weight, or 1.44 by volume.

S. M. W.

JULY, 1907

CHAPTER II.

INTRODUCTION.

General and historical facts. — The idea of utilizing the expansive force of gases produced by the explosion of a combustible mixture is doubtless as old as the invention of gunpowder. But the question remained largely one of speculation until it became known how cheaply to manufacture and store the combustible gases, and how to mix them in suitable proportions with air.

As knowledge concerning the mutual equivalence of mechanical work and heat became general, these vague ideas took form, and instead of burning the fuel at a very low efficiency in the furnace of a steam boiler, attempts were made to develop in engines, without the use of any intermediary substance, the potential energy contained in such combustibles as are suitable for the utilization, although somewhat imperfectly, of that part of the energy retained by steam in driving a steam engine.

It was to the use of illuminating gas, produced from the distillation of coal, that the first efforts were directed. Lebon described, in 1801, a mechanical apparatus in which illuminating gas and air, compressed in separate chambers, were mixed at the bottom of a double-acting cylinder and lighted, and in which the gases formed by combustion forced the piston to move backward and forward.

Later there appeared the system called the atmospheric system, that is still in use in some places. Within a cylinder equipped with a large air-cooling surface or surrounded

with a water jacket, and open at the top, a piston can move back and forth. A gas pipe is connected with the bottom of the cylinder. The proper amount of air is let in at the same time as the gas, then the mixture is lighted by contact with a flame constantly burning on the outside of the cylinder, and which penetrates it at the proper instant. An explosion is produced, and immediately the opening by which the flame enters is closed, while the piston is raised by the explosion. When the piston has reached its highest point, the burned gas escapes through a valve that at once closes. As the gases remaining in the cylinder cool, the pressure of the atmosphere forces the piston to descend. When equilibrium has been reëstablished, a valve set in the piston opens, and the piston continues to descend under the force of a powerful fly wheel and drives out the remnant of the burned gases. The fly wheel continues to draw the piston in an upward movement, air and combustible gas enter, and the cycle of operations continues so long as the gas supply is open.

Such are the two prototypes of explosion engines. These engines attracted the attention of engineers because they showed great practical advantages over the steam engines of that time.

Always ready to work, they required no expense in starting and no loss of time, a thing of the greatest importance to small plants requiring work of variable duration and at irregular intervals. Nevertheless, the presence of high temperatures, incompatible with the methods of lubrication then available, and the very rapid fluctuations in turning moment of the engine, made for a long time grave practical difficulties that delayed the hoped for progress. It was not till 1860 that the problem seemed to be solved by Lenoir, who invented a type of double-acting horizontal engine with a water jacket, but its consumption of gas

was excessive. Gradually it was seen that it is not advantageous to introduce the gas, as was done by Lenoir, during the time that the piston in its movement is increasing the capacity of the explosion chamber. So it was decided to introduce the mixture of previously proportioned and compressed air and gas into an extra clearance space, and explode it when the piston was at its lowest point. Next, in order to obviate the difficulties of keeping the packing in order, the cylinder was left open at one end and only one face of the piston was used.

Beau de Rochas made an important change in engines and greatly simplified them when he invented the four-cycle engine, which did away with the separate compressor. In this engine the piston during its initial rise draws in a combustible mixture properly prepared outside; then on its return stroke it compresses this mixture in a clearance space at the bottom of the cylinder. When the piston is at the end of its stroke the explosion of the mixture is produced, either by an electric spark or by the contact of the combustible mixture with an incandescent surface. There results a considerable increase of pressure that forces up the piston, against which the expanding hot gases continue to maintain an effective pressure; then the piston reverses its motion under the action of the fly wheel. A valve operated by the engine is opened, the still very hot burned gases are driven out, and the cycle is repeated.

It is seen that only a single impulse is produced to two complete revolutions of the shaft; that, moreover, the turning moment fluctuates very rapidly during the stroke. If then we wish to obtain a regular movement, even with small engines, we must use very heavy fly wheels unless high speeds are used. Finally, in order to avoid too rapid wearing of the engine, very long bearings must be used, as

much for the piston as for the piston rod and the main shaft.

The more explosive the mixture is, the more necessary are these conditions.

If rich mixtures are used in large engines, to secure regularity of motion and to avoid too rapid wear of the moving parts and possible danger of sudden breakdown, the use of single engines is commonly abandoned, in spite of the disadvantage of increased friction.

To begin with, for moderate sizes two cylinders are used, whose pistons move two cranks mounted at 180° on the main shaft, yielding an impulse for each revolution of the fly wheel. Similarly, even four cylinders may be attached to the shaft. In the latter case, in order not to complicate the valve-operating mechanism, generally the four cylinders are so connected to the shaft as to act like two separate two-cylinder engines.

In spite of the disadvantage of furnishing only one impulse to every four strokes of the piston, the Beau de Rochas four-cycle engine is most frequently used, although attempts are made to return to the two-cycle engine. It is still found in modern kerosene engines in which there is substituted for the explosion a continuous combustion at constant pressure or at constant temperature instead of at constant volume.

The use of illuminating gas is too expensive for large engines, even when the owner makes his own gas. Hence the use of explosion motors would not have developed extensively if illuminating gas were the only fuel available.

But Dowson changed the situation by the invention of his generator in which a current of steam and air is passed over red hot coal. Under these conditions from 2 kilograms of coal, 1.5 kilograms of steam, and 4.56 cubic

meters of air, there is formed a gas having the following general composition:

Carbon monoxide, CO	41	per cent
Hydrogen, H	21	"
Nitrogen, N	38	"
Total	100	"

This gas has a calorific power of 1710 calories per cubic meter, or 192 British thermal units per cubic foot.

The use of high compressions, which have been generally adopted to-day, permits the employment of still poorer combustible gases, such as blast furnace gas. The production of a ton of iron yields on the average 4500 cubic meters (160,000 cubic feet) having a calorific value of 800 to 1000 calories per cubic meter (90 to 110 British thermal units per cubic foot). Scarcely more than sixty per cent of the gas is used to warm the blast. There then remains 1800 cubic meters (64,000 cubic feet) for the production of power. While a steam engine requires 7.5 cubic meters (265 cubic feet) of gas per hour per horsepower, a gas engine consumes for the same work only 3 cubic meters (105 cubic feet). The favor gas engines have found with the owners of blast furnaces is therefore easily understood.

But gas pipes are not available everywhere; and even if they were at hand, there would still be great practical difficulties in utilizing the gas for engines destined for traffic.

The production of the explosive gas, either in the engine itself or just before its use, has been proposed. Carbide of calcium is the only known solid which can be used in this way to furnish a combustible gas; but the acetylene produced would be too expensive and probably too dangerous. The only things remaining then for use are the combustible liquids, which are besides very easy to store.

The combustible liquids easiest to use are alcohol and the various mineral hydrocarbons such as gasoline, kerosene, crude petroleum, and benzene. Gasoline is a fuel very easy to use. The same is true of benzene, but up to the present time its consumption is not very great. Kerosene and crude petroleum require special devices for their use. If suitable engines are employed, alcohol makes a good fuel provided its cost is not too great.

For several years a great effort has been made in Germany to develop the use of alcohol as a source of light, heat, and power, in order to increase the demand for agricultural products.

In France the government has attempted a like movement, in anticipation of the threatened injury the new sugar legislation is likely to have on the beet root industry in many sections of the country.

Two competitions, one national, in 1901, the other international, in 1902, organized by the French Minister of Agriculture, provided an opportunity for manufacturers to meet their competitors, and compare results. Unfortunately a great and sudden increase in the price of alcohol delayed the promised development in use of this combustible. It is clear that alcohol as an illuminant will be superior to kerosene, as long as we have not the means to use kerosene in incandescent lamps.

As a source of heat, from a physical point of view, it is comparable with its rival; for even if its calorific power is much weaker, it requires less air. In many cases its slight inferiority is offset by the fact that the products of its combustion are odorless, while gasoline and kerosene never completely burn, but yield products with a disagreeable odor.

As regards its use in engines, it appears from experiments made at the international competition in 1902, that the

thermal efficiency of alcohol may be increased until it very much exceeds that of its hydrocarbon rivals. Much has been said for and against the use of alcohol in motors. Its partisans declare it can be substituted, instantly and without any modification, for gasoline in any engine; that it does not leave any disagreeable odor or smoke. On the other hand, its opponents claim that it forms acid products that corrode the cylinders and suction valves so strongly as to make them adhere to their seats after cooling. Generally speaking, the praises and objections are not well founded; all depends on the circumstances of the use, and the manner of production of the mixture of air and explosive. In the following chapters we shall try to show the conditions necessary for its use; they have already been complied with by certain types of engines.

Although the title of this book is "Alcohol Engines," it seems fitting to include a comparison, as complete as possible, of alcohol and the various hydrocarbons as fuels, in order that the difficulties in the use of each may be understood.

In order to understand their effect, we must also study briefly certain parts of the engines, especially carbureters.

Finally, it will not be useless to review the laws, generally little understood by manufacturers, which relate to the phenomena of combustion.

CHAPTER III.

CONDITIONS AFFECTING COMBUSTION OF GASEOUS MIXTURES.

Governing and cooling of explosion engines. — The internal combustion engines that we are to study do not have any such reserve supply of energy as steam engines possess in the hot water of their boilers. Each explosion of the gaseous mixture introduced during the suction stroke must suffice to produce the required external work and to overcome the frictional resistance during the strokes when there is no useful impulse.

It results from this that the machine must be so designed that the motive impulse shall be appreciably greater than the resistance to be overcome. Hence the engine would tend to run faster and faster were there no governor either to cut out entirely from time to time a charge of the explosive mixture, or to reduce the quantity of each charge.

Under the first method of governing, known as the "hit-and-miss system," when the engine is running under load, the governor, if it is sensitive, will cause one miss between two series of consecutive explosions. On the contrary, if the engine is running without any appreciable load, there will be one explosion between two series of misses.

Under full load, the heat produced by the explosions would soon raise the temperature of the cylinder walls so high that the lubricating oil would decompose and burn. The gas itself might ignite during the compression stroke

and cause a pounding which would rapidly wear the mechanism, even if it did not stop the engine. Hence it is necessary to cool artificially the exterior surface of the cylinder.

In small motors, used in light vehicles, it is often considered sufficient to provide the walls of the cylinder with corrugations which serve, while the vehicle is in motion, to conduct the heat to the surrounding air. In large automobile engines and in stationary engines a water jacket is used to absorb the heat given to the walls. Sometimes the water is constantly renewed, sometimes the same mass is continuously circulated by the use of a thermosyphon or by a pump, and loses its heat in a cooling chamber, and sometimes the cylinder is immersed in a large quantity of water which heats to the boiling point and boils away, requiring to be renewed from time to time.

If the cooling surface of the combustion chamber is large, if the number of explosions is small, and if the combustion liberates but little heat, the metal of the cylinder will be but little heated, and the reaction will be approximately isothermal. If the cooling surface is small, if the number of misses is small, if the combustion is rapid and liberates much heat, the interior of the cylinder wall will be greatly heated; it may be assumed that during the very short time of combustion only a little heat is transferred to the cylinder wall and the reaction will be approximately adiabatic, that is to say, a reaction without transfer of heat to the surrounding medium.

Evidently neither of these two limits is ever reached, but in actual experience they are approached more or less. We shall see that the operation of the adiabatic reaction is essentially different from that of the isothermal reaction, and that accordingly as one extreme or the other is approached, the operation of the motor will vary greatly.

Isothermal reactions and adiabatic reactions. *Velocity and acceleration of the reactions.* — Let M represent the mass of a substance capable of entering into a reaction. Assume the reaction to take place either at constant volume or at constant pressure, let m be the mass which has entered into combination at the end of the time, t, measured from the beginning of the reaction, and m' the mass which has entered into combination at the end of the time, t'. Then, by definition, the *average velocity of reaction* is the fraction, $\frac{m' - m}{t' - t}$; and the *velocity of reaction*, v, at the time, t, is the limit of $\frac{m' - m}{t' - t}$, as $t' - t$ is indefinitely diminished.

In the same way the *acceleration of the reaction*, a, is the limit of the ratio, $\frac{v' - v}{t' - t}$, as the difference $t' - t$ decreases indefinitely.

Although the knowledge of dynamic chemistry is limited, yet the following laws may be stated:

First. *In the case of a limited reaction taking place either at constant volume or under constant pressure, the velocity of the reaction diminishes in proportion as the mass, "m," which has entered into combination, increases.*

Second. *If a state of equilibrium can be reached the speed of the reaction tends toward zero, in proportion as the mass, m, approaches the value, E, corresponding to this equilibrium.*

Third. *In general for any system, the value of m being given, the velocity of reaction increases very rapidly as the temperature increases, other things being equal.*

It must, however, be noted that the last law is applicable only if in the range of existing temperatures the reaction reaches its limit and becomes total, or else if the limit of reaction is independent of the temperature or increases with the temperature.

Acceleration in isothermal reaction. — In a chemical system capable of reaction, let a slight variation of composition be assumed as a result of this reaction which is taking place and which is accompanied by a slight increase of temperature. By the principle of superposition of small movements, let the mass, m, undergo a variation approaching its final value, m', without change of temperature; then let the temperature, T, change to the temperature, T', all at constant volume or at constant pressure.

From the preceding laws, during the first variation the velocity of the reaction has diminished; hence the decrease in velocity may be represented by $(-c)(m'-m)$. On the other hand, if the temperature rises, the velocity of the reaction increases; the increase of speed due to the change of temperature may be represented by $(+k)(T'-T)$.

Combining these two variations, we have,

$$v'-v = -c(m'-m) + k(T'-T) \quad . \quad . \quad . \quad . \quad (1)$$

But if the reaction is isothermal, $T'-T=0$, by definition. Hence, dividing both sides of the equation by $t'-t$,

$$\frac{v'-v}{t'-t} = -c\frac{m'-m}{t'-t}$$

or, passing to the limit,

$$a = -cv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence: *It is characteristic of an isothermal reaction that the acceleration is always negative.*

In chemical language the reaction is not an accelerating one but a diminishing one.

Acceleration in adiabatic reaction. — If a reaction takes place at constant temperature, a quantity of heat is set free equal to $l(m'-m)$, in which l represents the heat set free under like conditions by the reaction of unit weight

of the acting matter. According to the previous definition, this quantity of heat may be written, $lv\,(t' - t)$.

If the temperature alone should vary, the reagents would absorb a quantity of heat equal to $h\,(T' - T)$, h being the average specific heat of the system under the existing conditions of volume, pressure, and temperature.

The total heat given to the surrounding medium is then,

$$H' = lv\,(t' - t) - h\,(T' - T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

But when the reaction is adiabatic, by definition, no heat is transferred to the surrounding medium. Therefore, by transposition,

$$T' - T = \frac{lv}{h}\,(t' - t) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substituting this value in equation (1),

$$v' - v = -\,c\,(m' - m) + k\,\frac{lv}{h}\,(t' - t).$$

Whence, dividing both members by $(t' - t)$, and substituting a and v for their values, $\frac{v' - v}{t' - t}$, and $\frac{m' - m}{t' - t}$,

$$a = \left(-\,c + \frac{kl}{h}\right)v \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Since all the reactions with which we are concerned are exothermic, l is positive; we have also seen that k is positive by the third law on page 29, and h is positive by definition. Therefore: *In an adiabatic exothermic reaction the acceleration of the reaction is greater than in an isothermal reaction.*

Furthermore, the value of a for an adiabatic reaction, being the algebraic difference of two quantities, may be positive or negative according as $\frac{kl}{h}$ or c is the greater. In the former case the velocity of the reaction and the

corresponding elevation of temperature will continually increase and the action is said to be explosive.

It is evident that with the same initial temperature, pressure, or volume, and composition of mixture, the reaction may be either explosive or non-explosive according as the temperature is controlled. From this we shall later deduce certain conclusions relative to the shape to be given to engine cylinders, according to the pressure used and the nature of the explosive mixture.

It follows from the above that a reaction, which would be explosive in an enclosure impermeable to heat, may become non-explosive if it is made isothermal. It is to this reason that the great differences observed in the value of the ignition point of a mixture of oxy-hydrogen gas must be attributed. While according to Mallard and Le Chatelier, the explosion takes place at about 550° C., Mitscherlich after many variable results fixed on 674° as the ignition point of this mixture, while more recently A. Gautier and Helier, under almost isothermal conditions, have increased the point of ignition to 845°. The combination was almost complete.

An important thing to notice is that in the equation, $a = \left(- c + \frac{kl}{h}\right)v$, the quantity, h, representing the amount of heat absorbed by the total system in being warmed 1°, varies with the composition of the system. It will be a minimum when only the elements necessary for the reaction, and in their theoretic proportion, are present. It will increase in proportion as an excess of either of the reagents or an inert substance is added; moreover, this substance may be the product of a previous reaction.

Apparent equilibrium and reaction. — Investigations made on dissociation phenomena have accustomed us to the

ideas of chemical equilibrium, and of the influence of temperature, at constant pressure, upon the value of the ratio, $r = \frac{m}{M}$ of the mass combined to the mass that may enter into combination.

But there are a great number of chemical phenomena in which this ratio is limited, that is to say, in which, for a given temperature, only a part of the substances capable of reaction can be combined without their being decomposed at the temperature of combination. There is then a great difference between the two types of reaction. To distinguish them, this latter kind are said to constitute states of *equilibrium.**

The law as observed in numerous exothermic combinations may be characterized in the following manner:

Below a temperature, T_0, the compound formed is stable, and the constituent parts cannot combine.

Between the temperatures, T_0 and T_1, the compound formed is stable; the constituent parts can combine up to a certain limit that increases with the temperature.

Between temperatures T_1 and T_2, the compound formed is stable, and the constituent parts combine entirely. Above temperature T_2, the compound formed decomposes partially, and the constituent parts can combine in part. These two opposite reactions have necessarily as limits the same state of equilibrium. The higher the temperature, the more complete is the decomposition.

We recognize, in the last case, the law of dissociation of exothermic compounds.

In studying the isothermal action of heat upon a mix-

* Equilibrium as used in the following pages does not always mean a true chemical equilibrium, but in many places refers only to an apparent equilibrium.

ture of oxy-hydrogen gas, A. Gautier and Helier* established the fact that the reaction begins at 180° C., becomes appreciable at 200°, and can be continued to 845° without an explosion. The value, *r*, of the ratio between the mass of water actually formed and the possible mass increases rapidly with the temperature. Inside this interval from 180° to 845° water is undecomposable.

The following table gives the result of their studies:

Temperature.	*r*.	Temperature.	*r*.
180°C	0.0004	416°C	0.357
200°	0.0012	433°	0.3981
239°	0.013	498°	0.5638
260°	0.016	620°	0.8452
331°	0.0978	637°	0.8565
376°	0.2511	845°	0.961

Helier has shown that the limiting temperatures given above change if there is present a foreign gas or an excess of either of the component gases.

He has observed similarly a zone of temperatures in which there takes place a limited combustion of carbon monoxide with oxygen without the carbon dioxide being unstable, as indicated in the following table:

Temperature.	*r*.	Temperature.	*r*.
195°C.	0.0013	566°C.	0.1443
302°	0.0044	600°	0.2114
365°	0.0141	689°	0.4633
408°	0.0303	788°	0.603
468°	0.0464	855°	0.650
500°	0.062		

If for each mixture capable of presenting phenomena of this sort a curve is drawn having for abscissas the tem-

* A. Gautier and Helier, *Comptes Rendus*, vol. cxxii, page 566, 1896. Helier, *Annales de Chimie et de Physique*, 7th series, vol. x, page 521, 1897.

peratures, and for ordinates the values of r, see Fig. 1, this curve, LL', will start from a certain point on the axis of abscissas, L, which may be called the *point of reaction*. The curve will rise rapidly at first to become asymptotic to the horizontal line, SS', whose equation is $r = 1$. The space to the left of this curve is the general region of equilibrium; that to the right is the general region of active reaction.

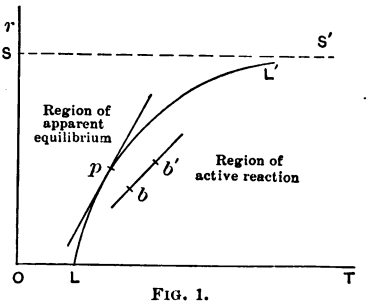


FIG. 1.

If we recall that the value of k in equation (5)

$$a = \left(-c + \frac{kl}{h}\right)v$$

increases usually with the temperature, and can cause an adiabatic reaction to pass from the non-explosive to the explosive form, it is easily apparent that there will often be in the region to the right of the curve two sub-regions: in the first the reaction will be characterized by a negative value of a, and will be non-explosive; in the second, a will be positive and the reaction will be explosive.

Moreover, in many cases, a is always negative and there can exist only non-explosive reactions.

When the two sub-regions exist, they are separated by a dividing curve, corresponding at every temperature to the value $a = 0$. Since the value of the term $\frac{kl}{h}$ varies simultaneously with the value of k and with the value of h, this dividing curve will depend simultaneously on the temperature and on the ratio of the amount actually present of the compound which is formed as a result of

the reaction, to the amount of the compound that would be present if the reaction were complete. It is immaterial whether the amount of the resulting compound actually present is formed as a result of reaction, or whether it is present in advance. The amount of neutral or inert foreign gas present will also have an effect.

In Fig. 2 the curve EE' separates for a given system, the region of non-explosive reactions from that of explosive reactions, if the latter can exist.

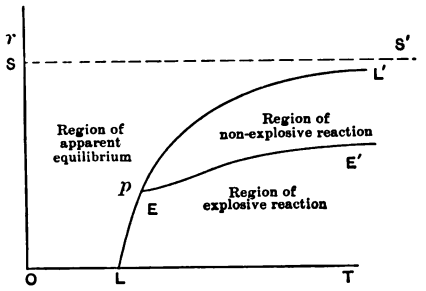


FIG. 2.

As the point L is called the point of reaction, the point E may be called the point of explosion.

Considering the curve LL', start with a point, p, of this curve, and suppose if possible the system to undergo an isothermal variation increasing the value of r. The new state would be represented by a point situated vertically above p, and, consequently, in the region of equilibrium. Hence no such isothermal reaction can be produced.

On the other hand, suppose the case of a pure adiabatic reaction.

The slope of the tangent to the curve LL' at the point p has for its value the limit of $\frac{r' - r}{T' - T}$. But in consequence of the position of the point p on the bounding curve LL' of the region of equilibrium, if some displacement should make the state represented in point p pass to a state represented in point p' of the same curve,

necessarily $v' - v = 0$. Then in conformity with equation (1):

$$c\,(m' - m) = k\,(T' - T)$$

or,

$$cM\,(r' - r) = k\,(T' - T):$$

consequently,

$$\text{tangent of } A = \frac{r' - r}{T' - T} = \frac{k}{cM}.$$

On the other hand, let the point p be moved in such a way as to bring it into position b, at a time t, and into position b', at a time t', by adiabatic reaction: the slope of the tangent to the curve, of which bb' is an element, is:

$$\text{tangent of } A' = \frac{r'_1 - r_1}{T'_1 - T_1}.$$

The fact that the reaction is adiabatic is expressed by placing in accordance with equation (4),

$$T'_1 - T_1 = \frac{lv}{h}(t' - t);$$

and since,

$$v\,(t' - t) = m' - m = M\,(r'_1 - r_1)$$

we may write

$$T'_1 - T_1 = \frac{l}{h} M\,(r'_1 - r_1):$$

whence,

$$\text{tangent of } A' = \frac{h}{lM}.$$

If it is found that the tangent of A' is greater than the tangent of A, that is to say, if $\frac{h}{l} > \frac{k}{c}$, or if $c > \frac{kl}{h}$, then the curve of reaction, after an infinitely small displacement, starting from a point on the boundary, LL', enters the region of equilibrium and the apparent equilibrium is stable.

If, on the contrary, $c < \frac{kl}{h}$, the curve of reaction enters

the region of active reaction. Hence the apparent equilibrium is unstable, or the slightest adiabatic change will cause an indefinite reaction and the values of both T and r will increase. Depending upon the size of tangent of A', or of $\frac{h}{l}$, the curve of reaction will be kept in the region of non-explosive reaction or will reach that of explosive action if the latter exists.

In accordance with the value given to h, the inequality, $c \gtrless \frac{kl}{h}$, may reverse in sense. Hence stable equilibrium may change to unstable equilibrium, or the inverse. It suffices to add to a combustible mixture a suitable quantity of neutral gas to render apparent equilibrium stable and prevent all reaction, other conditions being the same.

Since the curve, LL', is asymptotic to the horizontal line, SS', whose equation is $r = 1$, the tangent of A rapidly approaches zero as r increases. Hence, as r becomes larger, the chances of finding a state of equilibrium become greater.

In other words, if we consider the case of explosion engines, the greater the excess of air introduced or the greater the amount of burned gas that remains in the clearance space, the more difficult it is to produce the explosion.

Between the inequalities $\frac{h}{l} > \frac{k}{c}$ and $\frac{h}{l} < \frac{k}{c}$ lies the equality $\frac{h}{l} = \frac{k}{c}$. The point, p, on the curve, LL', which corresponds to this equation, separates that portion of the curve corresponding to stable equilibrium from the portion representing unstable equilibrium. Since, as shown above, in the vicinity of the asymptote the equilibrium boundary curve is stable, the stable portion corresponds to the por-

tion of LL' above the critical point; and the unstable portion to the part below.

Considering a state represented by a point very near LL' and to the right of it, if $\frac{h}{l} > \frac{k}{c}$, or $c > \frac{kl}{h}$, the acceleration of the reaction is negative, and the reaction is non-explosive. If, on the other hand, $\frac{h}{l} < \frac{k}{c}$, or $c < \frac{kl}{h}$, the reaction is explosive. If, then, the point taken is near the part of the curve, pL', the reaction will be non-explosive; when the point is near the part of the curve, Lp, the reaction will be explosive.

It is clear then that the bounding curves, LL' and EE', meet at the critical point, p, and that the field is divided as is shown in Fig. 2.

As the end aimed at is to realize very rapid combustion, in order that the cycle may be the largest possible, it is clear that the case of explosive combustion must be approached as nearly as possible. An attempt must then be made to render approximately real the case of adiabatic reactions, that is, to make k the largest possible; in other words, to maintain the highest temperature compatible with the good mechanical working of the engine, and its preservation.

It will, then, be necessary not to lower too far the temperature of the cylinder walls.

It will be necessary to diminish as much as possible the value of h by introducing only such excess of air as is necessary for practical combustion. Also the initial value of r must be diminished as much as possible by driving out as far as possible the consumed gases.

Relative dimensions of the cylinder. — Since explosive combustion can be produced only by avoiding isothermal reaction and approaching, as nearly as possible,

adiabatic reaction, the surface of contact of the combustion chamber with the cooling envelop must be diminished. In some kerosene engines, the cooling of the end of the cylinder is dispensed with, and self-ignition of the compressed mixture is secured, a thing that simplifies the machine; but if the work is irregular, cooling may take place and the combustion become incomplete or fail altogether.

This surface of contact may be diminished either by increase of pressure, care being taken to avoid self-ignition, or by giving to the ratio of the diameter to the length of the stroke, a value such that the surface of contact of the combustion chamber with the water jacket shall be the smallest possible *for the compression used.*

It may be conceived then how an engine very satisfactory with one fuel may, for no other reasons, become mediocre or inferior with another fuel.

Different shapes and different compressions are adopted according to the amount of heat set free from the combustion of the substance used, and even according to the power of the engine.

To determine the relative dimensions such that at the moment of explosion the cooling surface shall be a minimum for a given compression: Call V the volume of a cylinder, and n the ratio of the combustion chamber to the total volume of the cylinder; the volume of this chamber will then be nV.

Usually, on account of strength, the cylinder has a spherical end. Let x be the radius; y the distance from the piston at the end of its stroke to the center of the hemispherical head; S the area of cooling surface at the moment of ignition.

$$S = 2\pi x^2 + 2\pi xy$$

or,

$$\frac{S}{2\pi} = x + xy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

But $$nV = \tfrac{2}{3}\pi x^3 + \pi x^2 y \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Eliminating y between these two equations,

$$\frac{x^2}{3} + \frac{nV}{\pi x} = \frac{S}{2\pi}.$$

Differentiating with respect to x, considering V constant,

$$\frac{1}{2\pi}\frac{dS}{dx} = \frac{2x}{3} - \frac{nV}{\pi x^2} = \frac{2\pi x^3 - 3nV}{3\pi x^2} \quad . \quad . \quad . \quad (8)$$

This derivative is negative for negative values of x, and positive for very large positive values of x. Therefore S passes through a minimum determined by equating the derivative to zero.

Hence, $$\frac{2\pi x^3}{3} = nV \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and the combustion chamber ought to be formed solely of the hemisphere whose radius is x.

As it is customary to compare the bore of the cylinder with the stroke of the piston, let d equal the stroke. Then,

$$V = \frac{2}{3}\pi x^3 + \pi x^2 d \quad . \quad . \quad . \quad . \quad . \quad (10)$$

from which $$d = \frac{V}{\pi x^2} - \frac{2}{3}x,$$

or, $$\frac{d}{2x} = \frac{V}{2\pi x^3} - \frac{1}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

But from (9), $$\frac{V}{2\pi x^3} = \frac{1}{3n}.$$

Substituting this value in equation (11):

$$\frac{d}{2x} = \frac{1}{3n} - \frac{1}{3} = \frac{1-n}{3n}.$$

The following table gives the values of $\frac{d}{2x}$, for the values of n most in use:

n	$\frac{d}{2x}$
$\frac{1}{2}$	0.33
$\frac{1}{3}$	0.67
$\frac{1}{4}$	1.00
$\frac{1}{5}$	1.33
$\frac{1}{6}$	1.67
$\frac{1}{7}$	2.00
$\frac{1}{8}$	2.33

Consequently, the more difficult it is to explode the mixture the greater must be the pressure, and the larger must be the ratio of the piston stroke to the diameter of the cylinder.

It is seen that to explain the preference given to long cylinders by some makers of special alcohol engines, it is not necessary to give as a reason slow combustion or the expansion of the steam. The indicator diagrams taken from the greater part of the engines at full speed, indicate no trouble from slow combustion, provided the engine is operated under a strong compression, greater than that used with gasoline engines, and if the cylinder is not too much cooled. On the other hand, the hypothesis of an expansion of steam, that is often cited, doubtless from comparison with the action of steam engines, is not tenable because of the high temperature of the cylinder that makes the steam work much like a perfect gas.

The introduction of water into the cylinder, a thing that has been much recommended, can have for its aim only the use of greater compression or of warmer mixtures, without the risk of pre-ignition, since the vaporization of the water absorbs some heat; but at a constant compression and with a constant composition of the mixture, the maximum pressure of the explosion will be weaker.

It is proper to notice that if the speed of the engine is very rapid or if its power is great (in this case the ratio of the volume of the cylinder to the surface increases) it may happen that with the adoption of the above ratios the temperature on the interior surface of the cylinder, and on the non-cooled surface of the piston during operation at full load, will increase gradually to the point of producing self-ignition before the end of the compression stroke; or at least of producing changes in the combustible mixture. Some able builders have either diminished the compression in the large sizes of their engines, or for the same compression have diminished the ratio of the piston stroke to the bore, the nature of the explosive mixture remaining the same.

Influence of pressure. — Pressure, as well as temperature, plays a very important part in gaseous reactions, either indirectly or directly.

The more rapidly the gas is compressed and the less permeable to heat the confining chamber is, the more perceptible is the indirect action of pressure. To account for the importance of this indirect action under the conditions just described, let T_0 be the absolute initial temperature (Centigrade temperature increased by 273°), and T the temperature reached when the pressure has passed from the value P_0 to the final value P in an enclosure impermeable to heat. Suppose for the moment that the ratio of the specific heat of the gaseous system

under constant pressure to the specific heat at constant volume has a mean value, $K = 1.40$.

Then, $$\frac{T}{T_0} = \left(\frac{P}{P_0}\right)^{0.40}.$$

Suppose that the initial Centigrade temperature is 17° (63° F.); then $T_0 = 290°$ (522° F.), and placing $P_0 = 1$, we have:

P, in Atmospheres.	T.	Degrees Centigrade.	Degrees Fahrenheit.
1.5	333	60	140
2	382	109	228
3	450	177	319
4	505	232	450
5	552	279	534
6	594	321	610
7	631	358	676

In practice a part of the heat set free is communicated to the water jacket, but on the other hand the walls heated by the preceding explosion, warm up the gases during the first and the beginning of the second strokes. In any case, there is a considerable warming.

With industrial alcohol, the elevation of temperature so produced, while not great enough to cause ignition, is able to produce oxidation and harmful changes, as will be seen later.

On the other hand, pressure directly accelerates the reactions. This may be easily observed in eudiometric analyses. A combustion that would be dangerously explosive under ordinary pressure becomes non-explosive and without danger under reduced pressure. Inversely, a mixture that will not detonate when it is under very slight pressure will burn gently at a higher pressure, and if the pressure is increased slightly more an explosion with complete combustion will take place, just as if the temper-

ature had been raised by the addition of an easily combustible mixture.

Evidently, then, variations of pressure have the same effects as variations of temperature studied above. With a mixture of given composition, at a constant temperature but under a variable pressure, conditions of equilibrium would be met, next non-explosive reaction, then explosive reaction.

The direct and the indirect effects of pressure acting in the same way, the less explosive the mixture used, the smaller must be the ratio of the combustion chamber to the total cylinder. Unfortunately there is very little information on the subject of the influence of pressure on exothermic reactions. The clearest observations have been made on the subject of endothermic reactions.

Hautefeuille and Chapuis, (*Comptes Rendus,* vol. xci, page 552), have shown that ozone which under ordinary pressure is slowly decomposed into oxygen, may become explosive under strong pressure.

It is to the same influence of pressure that the action of fulminate of mercury in transforming a non-explosive reaction into an explosive one must be attributed. This action is a little more complex, for there is present at the same time a local increase of temperature with an abrupt compression.

At ordinary pressure acetylene gas submitted to the action of heat, or to a series of electric sparks, or to contact with a red hot platinum wire, is simply modified either by making polymeres or by being changed into hydrogen and carbon. At the most, if the general temperature is sufficiently raised, a glow is produced in the warmest parts of the tube. This glow is a proof of heat set free through polymerization. Fulminate of mercury produces only a local reaction.

Acetylene gas acts quite differently when it is compressed. Under a pressure of 137 centimeters of mercury, it detonates violently when it comes in contact with a red hot platinum wire. A priming of fulminate of mercury, containing 1 decigram of that substance, detonates acetylene gas under a pressure of 130 centimeters of mercury.

Limits of combustion. — It depends upon the pressure, the temperature, and their variations to which a gaseous mixture is submitted, as well as on its initial composition, whether the mixture presents a state of apparent equilibrium, or is the seat of a non-explosive reaction, or is explosive.

Under the same conditions of pressure and temperature, the region of apparent equilibrium may be entered from the region of reaction, generally at two points in the separating curve.

In the case of combustion there will ordinarily be two limits to the amount of oxygen in the mixture, between which the combustion of a homogeneous mixture is complete, and beyond which the combustion is incomplete or does not take place.

These limits vary considerably with variation in diameter of the eudiometer, the temperature, the pressure, and the length of the column of gas. They will also vary with the chemical nature of the body not combining, whether it is an excess of one of the bodies capable of reacting or whether it is a non-reacting body.

If in place of trying to approach adiabatic conditions, substantially isothermal conditions are taken, by the employment of a long, narrow eudiometer furnished with a cooling jacket; if, besides, a mixture close to the limit of combustion is used, and this is set on fire at the top of the tube by means of an electric spark, a slightly luminous sheet will be seen to descend more or less slowly toward

the bottom of the tube. This is called stratification of the flame and signifies that combustion is not complete.

In operating with hydrogen, which gives the least complicated reactions, it is observed that the quantity burned in the eudiometer is in a simple ratio to the total quantity of combustible gas when the mixture is in the vicinity of the limit of combustion. This ratio will be, for example, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$.

The experiments of Neyreneuf permit an explanation of this phenomenon. He used some long, narrow eudiometers, whose inner surfaces were covered with a thin coating of paraffine. Mixtures of oxygen and hydrogen near the limit of combustibility were lighted in the upper part of the tube by an electric spark. He observed that in the upper part of the tube regular rings were formed, caused by a melting of the paraffine, then no further action till a distance representing $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ the length of the tube from the top was reached. A vibratory movement had taken place, the combustion being a little more active at the points midway between the nodes, corresponding to a compression, than at the nodes corresponding to an expansion. The paraffine had melted at the crests. This incomplete propagation of combustion permitted the influence of the wall to have some effect, so much so that the mixture passed from the explosive phase at the point of contact of the spark to the phase of non-explosive combustion. But the explosive phase recurred at each crest of the vibrating gaseous column until the loss of temperature brought the curve of reaction down to the limit of equilibrium, at which point all action ceases.

This matter would have little interest if this phenomenon applied only to the case of narrow eudiometers. But a similar action takes place in a cylinder so large that the effect of the walls is negligible.

An experiment by Schloesing, rather difficult to perform, however, permits this phenomenon to be seen in a dark room and even to be made visible to an audience by a slight device.

This scientist introduced a rapid current of air through a large tube, slightly contracted at its upper end, into a large glass bell jar supported on blocks so as to allow a free escape of the gas. The jet strikes against a metal cap several centimeters from the orifice after having been submitted to an electric spark. A stream of hydrogen was introduced into the current of air and was gradually increased until a faint flame appeared at the extremity of the tube. The electric spark was immediately discontinued and soon the whole bell jar was filled with phosphorescent layers showing bands of intersection still more luminous, evidently due to slightly more intense local action. The reaction is, moreover, so weak that the bell jar is scarcely warmed.

The bands of intersection may be rendered more visible by introducing with the hydrogen a very small amount of phosphuretted hydrogen, but then the eye can no longer perceive the layers.

Hence with weak mixtures combustion is likely to be very incomplete. This may be obviated, as shown above, by increasing the pressure more and more in proportion as the mixture is naturally less explosive. It may also be avoided by a method of ignition which creates instantly throughout the whole mass an increase of pressure and considerable heat.

If a slow-burning mixture such as carbon monoxide and oxygen is lighted at the end of the tube, the eye follows easily the sheet of flame which moves slowly, and moreover the rise of temperature is slight. But let a small burning jet of the same mixture be projected by some

device throughout the entire mass of the mixture, and the explosion is sharp and the combustion complete.

This method has been used in engines by starting the explosion in the valve chamber where the mixture is relatively rich; if a contraction separates this chamber from the rest of the compression chamber a sudden powerful jet of flame is produced which instantly ignites the whole mass. Hence, there are produced very closely the conditions of an adiabatic reaction.

Complex mixture limits. — With combustible gases other than hydrogen, containing two or more elements, the phenomena of incomplete combustion are much more complex. The different elements are not equally combustible and the oxygen is shared between them, causing a progressive decomposition of the hydrocarbons. Finally, under the action of the heat set free, the different hydrocarbons originally present, or resulting from the first part of the reaction, may react upon each other.

In studying incomplete combustion of a mixture of oxy-hydrogen gas and carbon monoxide, Bunsen thought he had found the following law (*Méthodes gazometriques*, French translation, 1858, page 278): "When the molecules, a, of a homogeneous gaseous mixture have the choice of combining with the molecules, b and c, of two gases present in excess, there will be established between all these molecules an equilibrium such that the compounds $a + b$ and $a + c$, resulting from the combination of a with b and a with c, have a simple atomic ratio which depends upon the amounts of b and c present in excess; and this ratio varies abruptly with the amounts of excess present."

But Professor Hortsmann showed that this law was only accidental and that the regularity established could be accounted for by the presence of water vapor and its

dissociation products. He showed that a perfectly dry mixture of hydrogen, carbon monoxide, and oxygen undergoes a gradual combination not varying by sudden changes. Bunsen recognized the validity of this objection.

It will be shown later that in certain carbureters and during the compression stroke alcohol may produce certain hydrocarbons that are found in part in the exhaust gases. These same gases may also be produced by a deficiency of oxygen or by a lack of uniformity in the mixture.

Unfortunately there is but little known concerning incomplete combustion of bodies containing carbon and hydrogen. Nevertheless, here are some facts.

According to Gay-Lussac a mixture of 100 volumes of hydrogen with 900 volumes of oxygen burns incompletely when ignited by the electric spark, while methane, CH_4, still burns very well when to 100 volumes of this gas 950 volumes of oxygen are added (theoretical proportions are 100 volumes of CH_4 to 200 volumes of O). The amount of oxygen that can be used with methane is then greater than can be used with hydrogen. If less oxygen than the theoretic quantity is introduced, the inferior limit of combustion is gradually approached. With equal volumes there is still an explosion through the whole length of the testing tube, although the combustion cannot be complete. Below these proportions, there occurs only a slow combustion that can be followed by the eye, as when gas is ignited at the mouth of a testing tube.

Coquillion (*Comptes Rendus*, vol. lxxiii, page 709) found different limits, but by introducing an inert substance, nitrogen, which acts as a cooling and diluting agent.

If 1 volume of methane, CH_4, and 5 of air are mixed, nothing happens when they are subjected to the electric spark; with 1 part of methane and 6 of air an irregular

explosion is produced (the inferior limit of combustion through excess of methane); with 1 of methane and from 7 to 10 of air, the explosion becomes very distinct; if the proportion of air is increased to 12 or 15 volumes for 1 of methane, there is still an explosion, but a less and less active one. Methane ceases to explode with 16 volumes of air (the limit of combustion through excess of air).

Ethylene, C_2H_4, acts in practically the same way.

For ethane, C_2H_6, which theoretically requires 7 volumes of oxygen for 2 of ethane, the inferior mixture limit is 3 volumes of oxygen to 2 of ethane.

For acetylene, C_2H_2, which requires 5 volumes of oxygen for 2 of the gas, the inferior mixture limit is 1 volume of oxygen for 2 of acetylene.

So, as has already been noted, in a combustible gaseous mixture the presence of an excess of any one of the component gases, by absorbing a part of the heat set free, fixes the dividing line between the zone of explosion and that of non-explosion, also the line between the zone of non-explosion and that of apparent equilibrium.

Influence of neutral gases. — Naturally the same thing happens if a certain quantity of foreign or neutral gas is added to an explosive mixture. But, at least in some instances, the nature of the neutral gas modifies the limits of combustion, as the following experiments made by Bunsen show.

The following mixtures are explosive:

1 volume of oxy-hydrogen gas with 2.82 volumes of CO_2.

1 volume of oxy-hydrogen gas with 3.37 volumes of H.

1 volume of oxy-hydrogen gas with 9.35 volumes of O.

The following mixtures are incombustible:

1 volume of oxy-hydrogen gas with 2.89 volumes of CO_2.

1 volume of oxy-hydrogen gas with 3.93 volumes of H.

1 volume of oxy-hydrogen gas with 10.68 volumes of O.

It is seen that the anhydrous carbon dioxide has a considerable influence; this influence may be attributed to a cooling due to a partial dissociation of this gas; while the great conductibility of hydrogen may be considered as the cause of its bad influence.

In every case it is certainly harmful to allow an excess of the products of combustion to come in contact with the fresh charge in an engine. These experiments deserve to be repeated from a practical point of view, for the influence of a foreign body in causing the limit of combustion to vary is at times extraordinary, and suggests the action of a calalytic agent. Such is the case with traces of water vapor, which, without acting in any visible way in certain reactions, are nevertheless indispensable to their consummation.

Myers called attention to the fact that carbon does not burn in absolutely dry oxygen; Dixon, that a mixture of carbon monoxide and oxygen dried over anhydrous phosphorus loses its inflammability.

Baker has cited numerous reactions that are hastened or rendered possible by traces of moisture. To mention only the best known: the perfectly dry nitrogen dioxide does not react on dry oxygen to produce red vapors. Also hydrochloric acid gas and absolutely dry ammonia gas do not react upon each other; dry ammonium chloride is not changed by vaporization, but let a little moisture be introduced into the atmosphere, and in the first case a

combination and contraction takes place, and in the second case decomposition and expansion.

Trillat also showed that the presence of water is necessary in order that a mixture of air and glycerine vapor may keep up the incandescence of a platinum coil. If alcohol is used, the more water the alcohol contains the less heat this coil requires in a mixture of alcohol vapor and air.

Limits of combustibility. — The author made special experiments with the mixtures available for use in engines, to determine their combustibility at 100° C., and under a pressure of 760 millimeters.

For pure benzene, that theoretically requires, per gram, 10.71 litres of dry air at 10° C., to burn completely, the superior limit, through excess of air, is reached only if the quantity of air introduced is 2.2 times the quantity of air theoretically necessary. This is the highest ratio found in these experiments. The inferior limit through excess of benzene must be very low, for combustion is still observed when the ratio of the air introduced to the air necessary falls as low as 0.27. Just as in Coquillion's experiments, it would seem that the limit corresponds to the quantity of oxygen capable of burning the hydrogen, although there is no noticeable deposit of soot.

Ninety-five per cent alcohol requires per gram 6.757 litres of dry air at 10° C. Under the conditions of the experiment the mixture is only combustible if the air introduced does not appreciably exceed 1.5 times, and does not fall below 0.34 times the quantity theoretically necessary.

Ninety per cent alcohol requires per gram 6.216 litres of dry air at 10°C. Practically the same limits of combustibility are found.

Eighty-five per cent alcohol requires per gram 5.784 litres of dry air at 10 ° C. The limit of combustibility

through excess of air is the same as above. The inferior limit appears when the ratio of air introduced to air necessary lies between 0.40 and 0.45.

Alcohol carburated by benzene gives practically the same limits.

With gasoline, recourse was had to vaporization by bubbling air through the liquid in a manner of which examples will be given later. One of the principal elements, hexane, is almost exclusively extracted by the air within the limits of temperature employed. Within the above conditions of temperature the limit of combustibility through excess of air is reached when the ratio of the introduced air to the air theoretically necessary is in the vicinity of 1.84. The inferior limit, through excess of the hexane, is difficult to determine exactly; probably the ratio lies between 0.4 and 0.5.

To sum up: Within the conditions of the experiments the superior limits of combustibility vary very little for the greater part of the industrial mixtures studied; the inferior limits vary still less, except in the case of pure benzene.

The author's studies on combustible vapors also prove, as Bunsen pointed out, that in the vicinity of the superior limit of combustibility by excess of air, a very slight variation is required in the relative proportions of the oxygen and the combustible to pass from absolute incombustibility (at a given temperature and pressure) to a perfect combustibility. Examples of this will be seen in the tables concerning the velocity of flame propagation.

CHAPTER IV.

PHENOMENA OF COMBUSTION OF GASEOUS MIXTURES.

Propagation of combustion. — The velocity with which combustion is propagated plays an important part in all explosion engines in which ignition is produced by the combustion of the gases in an incandescent tube heated by an independent burner. If the tube is, as usual, in communication with the cylinder, during the compression stroke, the fresh gas presses to the end of the tube the burned gases remaining from the previous explosion. The velocity of the flame propagation may, at most, only equal the velocity with which the new combustible layers enter the tube, since when the piston reaches the dead point the flame returns to produce the explosion in the compression chamber before the piston commences its return stroke.

A very brief but measurable time passes before the ignition is transmitted to the mixture. Hence, it is advantageous to give a certain advance to the ignition in order that the total mass may take fire when the piston is at the dead point. If the ignition is produced too late, the volume of the chamber will have begun to increase and in consequence the pressure due to the explosion will be diminished and the useful work will be decreased. If, on the contrary, the ignition is too early, a resistant force will be produced and again a diminution of the useful work; in addition to which there will be unusual wear and tear on the engine.

The various combustible mixtures are far from having the same point of ignition, or the same velocity of propagation of combustion; hence it is expedient to regulate the length of the incandescent tube so that ignition may take place in the compression chamber at precisely the most favorable moment. Consequently it is necessary, at the same time, to take into consideration the quantity of burned gases remaining in the tube, the pressure at the end of the compression stroke, and the velocity of the propagation of the combustion.

It can be seen that many conditions not easy to determine exist. Generally this difficulty is obviated, in the case of an engine that always uses the same combustible, by trying different lengths for the incandescent tube until that length is reached which yields the maximum power. This result is generally attained by the use of washers.

If electric ignition is employed there is still uncertainty, for in order to cause an explosion in a given engine at a fixed time, the volume of gas ignited must be great enough to give the required elevation of temperature, and the velocity of flame propagation must be such that general ignition takes place at the moment when the piston is at the end of its stroke. Consequently the problem is very complex.

The velocity of the flame propagation, as we shall see, is very difficult to determine; moreover, in practice it is necessary to take into account the heat produced and the explosive power of the mixture. Bunsen tried to solve the main problem by eliminating the minor ones. He allowed the explosive mixtures to escape through a small orifice of a known diameter in a thin wall. He ignited the mixture that he released with sufficient velocity to cause the gas to burn on the exterior of the tube. He then gradually decreased the velocity of the flow until the

flame entered the tube. This retreat of the flame can only take place at the moment when the velocity of efflux becomes barely less than the velocity of propagation of the combustion. If, then, v is called the velocity of flame propagation, d, the diameter of the opening in the thin wall through which the gaseous current flows, and V the volume of gas that escapes at the given pressure in t seconds,

$$v = \frac{4V}{\pi d^2 t}.$$

Bunsen, in applying this method to pure oxy-hydrogen gas, found a velocity of flame propagation equal to 34 meters a second; with the mixture CO + O the velocity was only 1 meter.

In Michelson's experiments (*Zeitschrift für physicalische Chemie*, vol. iii, page 489) the influence of extraneous conditions is much more apparent, and the difference between the results obtained by this observer and those furnished by Bunsen show how important this influence is. Michelson went to work after quite a different manner; the gaseous mixture flowed into a tube with such a velocity that the combustion could no longer retreat. To accomplish this he employed a quite long tube in which, by the use of a stopcock controlling the gaseous flow, he succeeded in confining the flame to a fixed zone. In this case the velocity, u, of flame propagation in centimeters per second is deduced from the equation.

$$V = Su$$

in which V represents, in cubic centimeters, the volume of gas flowing per second, and S the cross section of the tube in square centimeters.

In these experiments Michelson studied the influence of the dilution of the theoretic mixture, on the velocity of propagation at constant pressure.

If the per cent by volume of the combustible gas in the total mixture is represented by n, according to Michelson the following results are obtained:

CARBON MONOXIDE AND OXYGEN.

Values of n.	Values of u.	Values of n.	Values of u.
25	30 centimeters	60	84 centimetres
30	40	65	88
35	49	70	91
40	58	75	91
45	66	80	85
50	73	85	70
55	80	90	45
		95	20
HYDROGEN AND OXYGEN.			
19.4	121	83.8	58.2
21.8	151	86.9	44

According to these experiments, the maximum velocity of flame propagation does not correspond to the mixture for which the two gases are exactly in the ratio corresponding to the theoretic combination.

It is clear that the divergence between the results obtained by Bunsen, and those furnished by Michelson show that one or the other of them neglected some essential factors affecting the phenomenon. Whether one case or the other is more nearly approached under any given circumstances depends on the conditions of the combustion. If the work is carried on in the open air, and the structural conditions of a Bunsen burner are to be calculated, Bunsen's results, as first given, must be used. In the case of an incandescent tube explosion engine the results of Michelson will probably be better. There are still new experiments to try on this subject.

The problem appears to be much more complex than the

one assumed by these two scientists. Judging from the contradiction between the two observers, it is very probable that the velocity of flame propagation depends, at the same time, on the maximum temperature evolved by the combustion, T_c, on the temperature necessary for ignition, T_i, on the initial temperature of the mixture, T, on the conductivity for heat, C, and on the specific heat of the mixture, h.

Consider with Bunsen a stratum that has just burned, and which has reached the temperature, T_c; through giving up heat to an adjoining and as yet unburned stratum of the mass, a fall of temperature has taken place to $T_c - x$, while the unburned stratum has risen in temperature to $T + x$. The rise in temperature during a unit of time will be expressed by the equation,

$$\frac{dx}{dt} = \frac{C}{h}[T_c - x) - (T + x)] = \frac{C}{h}(T_c - T - 2x).$$

Integration of this equation gives natural log $(T_c - T - 2x) = -\frac{2C}{h}t +$ a constant.

For $t = 0$, x must $= 0$. Therefore, the constant = natural log $(T_c - T)$.

Whence, $t = \frac{h}{2C}$ natural log $\frac{T_c - T}{T_c - T - 2x}$.

Since the value of x is the heat that must be added to T to increase it to T_i, the temperature of ignition, the time for transmitting ignition and, consequently, also the velocity of ignition, which is inversely proportional to it, vary rapidly with the initial temperature, T. If $2x = T_c - T$, it is even possible for the time of ignition to become infinite.

Hence, the velocity of propagation of ignition, even under experimental conditions, is extremely variable,

depending as it does on the composition of the mixture which determines the temperatures of ignition and combustion, on the initial temperature, and on the conditions of external loss of heat.

The only thing that can be done is to determine under conditions as identical as possible the influence of the composition of known mixtures upon the velocity of flame propagation.

In the case of engines we have seen that the state of rest or of motion of the combustible mixture has an important effect by varying the pressure of the portion in contact with the burning zone; that, moreover, the temperature of reaction and the acceleration of the reaction differ materially according as the action is isothermal or adiabatic.

Theoretical speculations are, then, insufficient to solve a problem so indeterminate; experiments are necessary in every case. Not being acquainted with any investigations on the conditions of the combustion of mixtures of air and combustible vapors, often complex, the author used for this purpose a mechanism a little more intricate than Bunsen's, but which, on the one hand, enables us to measure much smaller velocities, and, on the other hand, to avoid all error due to a partial condensation of the vapors.

In the chapter relative to the experiments on carbureting, whether by trickling or bubbling, the necessary data may be found. We shall here merely mention what concerns gasoline. At a temperature between 10° and 40° C. (50° to 104° F.), the air bubbling through gasoline, that is frequently renewed, carries away hardly anything except hexane, with some traces of butane and pentane. We have found that, calculating the whole as hexane, 100 liters of dry air measured at 10° C. under a pressure of 760 millimeters, takes up the following quantities of hexane at different temperatures:

Temperature.		Grams of Hexane Vaporized.
Centigrade.	*Fahrenheit.*	
12.2	54	29.44
14.8	59	30.63
16	61	31.32
18	64	32.50
20	68	35.37
22	72	36.10
24	75	37.74

Such mixtures would be too rich in combustible. To obtain mixtures for experiment, a given quantity of dry air is mixed with this rich gas. This air is warmed to the same temperature as the gas by passing through a long metallic coil immersed in the same bath as the bubbler. The gaseous mixture was rendered homogeneous by passing it through a copper tube also plunged in the bath, and nearly filled by a tightly wound roll of copper gauze intended to mix the gas and to prevent any working back of the flame. This tube was closed at the end by a thin disk pierced with four holes 0.4 millimeter in diameter. One of these holes was practically in the center of the disk, the others near the periphery. The copper tube was fastened by strong rubber to a glass tube 2.1 centimeters in diameter, and 75 centimeters long, surrounded by a steam bath with a temperature of 100° C.

The richness in vapor of the current of air bubbling through the liquid was regulated by varying the temperature of the bath. The current of additional air was under control, and the velocity of the air in each current was accurately measured.

An attempt was made to regulate the experiment in such a manner that the flame should be produced on the inside of the glass tube, but nearly at its extremity, so as to avoid, on the one hand, a mixture with an excess of air, and, on the other, the action of the products of combustion.

Since the velocity of flame propagation varies between rather wide limits, as the subsequent tables show, the required conditions were realized by attaching at the end of the large tube, by means of good cork stoppers, different sized pipes for the combustion to take place in. Pipes with the following cross sections were used:

No. 1	3.800 square centimeters
No. 2	0.785 square centimeters
No. 3	0.283 square centimeters.

If the flame burned outside the pipe, either the mixture was incombustible through excess of vapor and the flame showed a red point, or the velocity of the current of air was too great, in which case the flame was blue or green and retreated into the tube when its size was increased. If in the latter case the velocity of the current was less than the velocity of flame transmission the flame retreated into and moved through the entire length of the large tube. If the mixture was very combustible the flame formed a very thin blue layer and changed its place almost instantly; if the mixture was less combustible the flame was green and moved more slowly; when the mixture bordered on the limits of combustibility through excess of vapor the flame was green terminated by a reddish tinge, which sometimes became red before the combustibility became zero. In this case, generally a slight deposit of soot was made. Consequently the absence of smoke from the exhaust pipe of an engine shows merely that the extreme limit of combustibility has not been reached.

If the velocity of flame propagation and that of the air current are equal, the flame is seen to remain for a short time inside the small tube, which soon warms up and the rise of temperature hastens the reaction, the burning zone

fluctuates in the small tube, and abruptly enters the large tube where the velocity is less.

When the velocity of this retreat is not too great, it passes through a minimum, near the middle of the large tube, then increases from this point to the orifices opening from the copper tube. So, as Bunsen showed, the presence of the products of combustion retards the velocity of flame propagation, which perceptibly regains its value in proportion as an influx of fresh gas comes in to enrich the mass. The great differences that exist between the results of Michelson and those of Bunsen are thus explained. The following tables show the principal results of the author's experiments on industrial explosive mixtures. As usual, the results with gasoline have been calculated on the assumption that it may be represented by hexane.

PURE BENZENE.

Quantity of Benzene Vapor Carried by One Liter of Air Measured at 10° C. Under a Pressure of 700 Millimeters.	Ratio of the Air Introduced to the Air Necessary.	Maximum Velocity Observed.	Other Velocities Observed.	Remarks.
Grams.		*Meters.*	*Meters.*	
0.037	2.3	0.00	. . .	Incombustible.
0.046	1.94	1.13	. . .	Blue flame.
0.050	1.86	1.30	. . .	Blue flame.
0.057	1.63	1.29	1.04	Blue flame.
0.061	1.51	. . .	1.11	Blue flame.
0.070	1.33	. . .	1.12	Blue flame.
0.085	1.09	1.12	0.80	Blue flame.
0.094	0.98	1.04	<0.95	Blue flame.
0.104	0.89	. . .	0.65	Green flame.
0.110	0.84	∠0.60	. . .	Green flame.
0.124	0.76	∠0.53	≤0.23	Green and red flame.
0.153	0.61	0.55	. . .	Green and red flame.
0.211	0.44	0.25	. . .	Red flame.

Soot appeared only in the last two cases. Hence, up to that point the incomplete combustion had taken place without the separation of carbon.

PURE ALCOHOL OF VARIOUS STRENGTHS.

Quantity of 95 per cent Alcohol Vapor Carried by One Liter of Air Measured at 10° C. and Under a Pressure of 760 Millimeters.	Ratio of the Air Introduced to the Air Necessary.	Maximum Velocity Observed.	Other Velocities Observed.	Remarks.
PURE 95 PER CENT ALCOHOL.				
Grams.		*Meters.*	*Meters.*	
0.096	1.60	0.00	. . .	Incombustible.
0.100	1.53	1.00	0.10	Blue flame.
0.120	1.24	0.97	. . .	Blue flame
0.130	1.02	0.76	0.57	Green flame.
0.291	0.51	0.10	. . .	Green flame.
0.334	0.44	0.07	. . .	Green and red flame.
0.428	0.37	0.00	. . .	Incombustible.
PURE 90 PER CENT ALCOHOL.*				
0.0915	1.82	0.00	. . .	Incombustible.
0.0940	1.77	0.31	0.00	Almost incombustible.
0.104	1.60	0.31	0.14	Blue flame.
0.116	1.43	1.00	. . .	Blue flame.
0.129	1.36	1.04	. . .	Blue flame.
0.133	1.25	1.00	. . .	Blue flame.
0.172	0.97	0.70	. . .	Blue flame.
0.262	0.63	0.20	. . .	Green flame.
PURE 85 PER CENT ALCOHOL.				
0.1145	1.56	0.00	. . .	Incombustible.
0.1257	1.42	0.35	. . .	Blue flame.
0.1424	1.23	0.45	. . .	Blue flame.
0.2880	0.62	0.34	. . .	Green flame.
0.3200	0.55	0.28	. . .	Green flame.
0.3312	0.53	0.12	. . .	Green flame.

* The case of 90 per cent alcohol may possibly be explained by the experiments of Trillat on the great ease of oxidation in the presence of water.

NINETY PER CENT ALCOHOL MIXED WITH BENZENE (FIRST SERIES).

Per Cent of Benzene by Volume in the Mixture in the Liquid State.	Quantities of Vapor Carried by One Liter of Dry Air, Measured at 10° C. under a Pressure of 700 Millimeters.			Ratio of the Air Introduced to the Air Necessary.	Maximum Velocity Observed.	Remarks.
	Benzene.	90 Per Cent Alcohol.	Total.			
	Grams.	*Grams.*	*Grams.*		*Meters.*	
33.14	0.02658	0.04777	0.07435	1.77	0.00	Incombustible.
33.11	0.02773	0.05277	0.08050	1.49	0.37	Blue flame.
54.54	0.04757	0.03721	0.08478	1.36	1.15	Blue flame.
47.26	0.04546	0.04782	0.09328	1.27	1.14	Blue flame.
45.84	0.04350	0.08261	0.12601	0.98	0.68	Blue flame.
48.89	0.05046	0.05841	0.10887	0.70	1.15	Blue and green flame.
46.98	0.05754	0.06129	0.11883	0.63	0.79	Green flame.
42.34	0.05613	0.12209	0.17822	0.55	0.55	Blue flame.
33.36	0.08323	0.15679	0.24002	0.53	1.06	Blue flame.
49.94	0.11212	0.10525	0.21737	0.53	0.08	Green and red flame.
35.19	0.08929	0.15508	0.24437	0.52	0.99	Green flame.

NINETY PER CENT ALCOHOL MIXED WITH BENZENE (SECOND SERIES).

Per Cent of Benzene by Volume in the Mixture in the Liquid State.	Quantities of Vapor carried by One Liter of Dry Air, Measured at 10° C. under a Pressure of 700 Millimeters.			Ratio of the Air Introduced to the Air Necessary.	Maximum Velocity Observed.	Remarks.
	Benzene.	90 Per Cent Alcohol.	Total.			
	Grams.	*Grams.*	*Grams.*		*Meters.*	
58.20	0.05593	0.03763	0.09356	1.20	0.34	Blue and green flame.
66.54	0.06772	0.03196	0.09968	1.08	0.81	Green and red flame.
71.40	0.07638	0.02833	0.10471	1.00	0.72	Green and red flame.
63.41	0.07347	0.03996	0.11343	0.96	0.69	Green and red flame.
58.82	0.09237	0.06093	0.15330	0.73	0.40	Red flame.
70.40	0.08905	0.03521	0.12426	0.67	0.06	Red flame.
67.72	0.11891	0.05340	0.17231	0.62	0.05	Red flame.
60.21	0.11961	0.07446	0.19407	0.57	0.08	Green and red flame.
70.71	0.16511	0.06606	0.23117	0.46	0.00	Incombustible.

GASOLINE.

Quantity of Vapor Carried by one Liter of Dry Air Measured at 10° C. under a Pressure of 760 Millimeters.	Ratio of Air Introduced to Air Necessary.	Maximum Velocity Observed.	Other Velocities Observed.	Remarks.
Grams		*Meters*	*Meters*	
0.037	2.22	0.33	0.07	Almost incombustible.
0.038	2.19	0.00	. .	Incombustible.
0.044	1.85	0.30	. .	Slightly combustible.
0.045	1.83	0.00	. .	Incombustible.
0.048	1.76	0.88	. .	Blue flame.
0.056	1.49	0.94	. .	Blue flame.
0.059	1.49	. .	0.76	Blue flame.
0.061	1.35	1.10	. .	Blue flame.
0.069	1.22	. .	0.92	Blue flame.
0.070	1.18	1.07	. .	Blue flame.
0.075	1.11	. .	≥ 0.38	Blue and green flame.
0.077	1.08	. .	0.33	Blue and green flame.
0.079	1.08	0.56	. .	Green flame.
0.079	1.06	0.65	. .	Blue flame.
0.082	1.01	0.53	. .	Green and red flame.
0.085	0.98	0.31	. .	Green and red flame.
0.097	0.87	0.63	. .	Blue flame.
0.101	0.83	0.05	. .	Green flame.
0.115	0.73	0.04	. .	Green flame.
0.122	0.68	. .	0.00	Incombustible.
0.125	0.67	0.04	. .	Green and red flame.
0.129	0.61	0.02	. .	Red flame.
0.150	0.55	0.02	. .	Red flame.
0.153	0.54	0.00	. .	Incombustible.

A comparison of the preceding tables shows that under the conditions of the experiment the ratio of the air introduced to the air theoretically necessary, producing the highest velocity of flame propagation, is in the vicinity of 1.3, whatever may be the combustible. The different combustibles do not act in the same way. In some of them the velocity of flame propagation remains nearly constant while this ratio varies considerably until it becomes quite different from that which corresponds to total combustion. In others, such as hexane extracted by

bubbling air through gasoline, the velocity decreases very rapidly when the ratio of air used to theoretical air becomes less than 1.3.

In pure benzene the limits of combustibility are very far apart.

The mixture of 90 per cent alcohol and benzene shows some very strange peculiarities. The velocity of flame transmission remains fairly constant for mixtures poor in benzene; when the ratio of air introduced to air necessary varies considerably below the normal, then the velocity decreases abruptly to zero. It would seem that benzene having a heat of combustion much greater than 90 per cent alcohol ought to increase the velocity of flame transmission. It does this only, and even then but little, in mixtures rich in air. In mixtures poor in air, the opposite takes place. This fact may be due to incomplete decomposition of the very hot mixtures. It would, however, require a very careful analysis of the products of combustion to solve the problem. The means necessary for this research were not at hand, so the question had to be laid aside.

As will be seen in the chapter entitled "Actual combustion in engines," it was found from the tests at the international competition of May, 1902, that the most favorable ratio of air introduced to air necessary, lies, for alcohol engines, between 1.5 and 1.7. The author's experiments show that at a temperature of 100° C and under a pressure of 760 millimeters the mixtures thus prepared are incombustible. It would be advantageous then to take up again this experiment under adiabatic conditions, and at a pressure and temperature more nearly that reached in engines at the end of the compression stroke.

However it may be, the comparison of the author's results with those of Bunsen, presents interesting coinci-

dences. The velocities of ignition of the mixtures studied are very nearly identical with that of the carbon monoxide and oxygen mixture.

Near the limit of combustibility through excess of air, a very slight variation of composition is enough to cause an incombustible mixture to change to a perfectly combustible mixture, that burns rapidly and with a pale blue flame.

There is no evidence that the maximum velocities established would have the same relative values under the influence of temperatures and pressures used in engines and which will be calculated later. It is probable that in this condition is found one of the principal reasons that lead makers of engines to choose different compressions for the various fuels.

Temperature of ignition. — Bunsen defined the temperature of ignition as the lowest temperature capable of communicating to the constituent parts of a gaseous mixture the ability to combine abruptly.

According to what has been said in Chapter III, this temperature is not fixed, but depends on the more or less isothermal or the more or less adiabatic conditions of the reaction.

Suppose that in a gaseous mass containing substances capable of reacting, a gaseous layer is raised to the temperature of combustion by an exterior cause; reaction will be produced and the heat of the combustion will raise the temperature, unless the conditions are absolutely isothermal, but as this condition is never met in practice it may be ignored.

If the elevation of temperature is sufficient to cause the ignition of the contiguous stratum, the temperature communicated is superior to the temperature of ignition; if the reverse is true, the temperature is lower than the temper-

ature of ignition. Now, without changing the external conditions, the temperature developed by the combustion of a mixture can be lowered by adding to it the proper quantity of a neutral gas; thus a mixture may be created that becomes incombustible, and there may be closely determined for a combustible mixture such relative proportions that a very small addition of incombustible gas to the mixture, easily combustible, makes the mixture completely incombustible, as the following experiments of Bunsen on oxy-hydrogen gas show:

MIXTURE.

	Mixture. Incombustible.	Mixture. Combustible.
	Per Cent.	Per Cent.
Carbon dioxide	74.21	73.83
Oxy-hydrogen gas . . .	25.79	26.17
	100.00	100.00
Oxygen	91.28	90.34
Oxy-hydrogen gas . . .	8.72	9.66
	100.00	100.00

In experiments of this sort, under closely defined conditions, the problem of the temperature of ignition leads to the investigation of the temperature attained in the combustion of a definite mixture.

Heat of combustion. — The temperature of combustion may be directly determined. Mallard and Le Chatelier (*Comptes Rendus*, vol. xciii, page 104) found that carbon monoxide, burned in oxygen, produced a temperature of 3200° C. (5800° F.); burned in air it reached a temperature of 2050° C. (3700°F). But as the apparatus necessary for this direct measurement is generally not at hand, the temperature to which the products of combustion may be raised, can be determined theoretically, at least approximately. If Q represents the heat produced by the com-

bustion of 1 kilogram of the combustible body, and h represents the mean specific heat of the mixture produced by its combustion, the rise of temperature will be represented by the equation

$$D = \frac{Q}{h}.$$

It is necessary to distinguish between the heat produced at a constant volume (as in the bomb calorimeter or the explosion in the compression chamber of an engine at the end of the stroke) and the heat produced under constant pressure (case of combustion of a flame); the latter is the case generally measured and recorded in the tables.

A change may be made from the second to the first, as follows:

The laws of Gay-Lussac and Avogadro yield the approximate equation

$$APV = 2\,T$$

in which A represents the reciprocal of the mechanical equivalent of heat, V the volume of the kilogram molecule, and T the absolute temperature. Supposing the centigrade temperature to be 17°, then $T = 290°$, and consequently

$$APV = 580.$$

As an example, consider the case of carbon monoxide. Under constant pressure the molecular heat of combustion (per kilogram molecule) of carbon monoxide ($CO = 28$) has been found to be 68,200 calories.

But according to the equation $CO + O = CO_2$ a diminution of the volume equal to a half molecule is produced by the combustion. Work is then produced giving an amount of heat equal to $\frac{580}{2} = 290$. If then the combustion had taken place at constant volume, as in the bomb, the molecular heat developed would have been 68,200 –

290 = 67,910 calories. This is the number to take in the case of an explosion.

The following table gives the molecular heat of combustion both at constant pressure and at constant volume (per kilogram molecule) and the heat of combustion per kilogram for a number of combustible substances:

Substance.	Symbol.	Molecular Weight.	Molecular Heat.		Heat of Combustion per Kilogram.	
			At Constant Pressure.	At Constant Volume.	At Constant Pressure.	At Constant Volume.
					Calories.	*Calories.*
Hydrogen	H	2	58,200	57,910	29,100	28,950
Amorphous carbon	C	12	97,000	97,000	8,083	8,083
Carbon monoxide	CO	28	68,200	67,910	2,432	2,425
Acetylene	C_2H_2	26	318,190	318,680	12,234	12,280
Ethylene	C_2H_4	28	341,400	341,980	12,193	21,214
Ethane	C_2H_6	30	389,300	389,880	12,977	12,996
Methane	CH_4	16	213,500	213,500	13,344	13,344
Allylene	C_3H_4	40	466,500	467,660	11,662	11,691
Propylene	C_3H_6	42	507,300	508,460	12,078	12,106
Propane	C_3H_8	44	553,500	554,460	12,580	12,600
Amylene	C_5H_{10}	70	804,400	806,720	11,490	11,525
Benzene	C_6H_6	78	776,000	778,940	9,950	9,985
Naphhtalene	$C_{10}H_8$	128	1,242,700	1,247,920	9,708	9,749
Methyl alcohol	CH_4O	32	170,000	170,000	5,312	5,312
Ethyl alcohol	C_2H_6O	46	324,500	325,080	7,054	7,067
Acetone	C_3H_6O	58	424,000	425,160	7,310	7,330
Aldehyde	C_2H_4O	44	269,500	270,080	6,125	6,138

According to this table, 90 per cent by volume (85.70 per cent by weight) ethyl alcohol under constant pressure produces 6045 calories of heat and at constant volume 6056 calories per kilogram.

Ninety per cent by volume (86.3 per cent by weight) methyl alcohol produces in both cases 4594 calories per kilogram.

The mixture of 10 volumes of 90 per cent ethyl alcohol and 1 volume of 90 per cent methyl alcohol, which is practically French denatured alcohol, produces 5923 calories.

From experiments with the bomb calorimeter, a number very close to 5906 has been found for alcohol denatured by the French excise. This alcohol was used in the official tests at the competition of November, 1901.

The same alcohol mixed with an equal volume of 90 per cent benzene produced in the bomb 7878 calories.

When the heat of combustion of the heavy hydrocarbons cannot be directly determined, according to Staby it may be assumed that, the specific weight of vapor in kilograms per cubic meter being e, the heat of combustion is practically represented by $1000 + 10{,}500e$, in calories per cubic meter measured at 0° C and under the pressure 760 millimeters of mercury.

According to Redtenbacher, who has corrected the old formula of Dulong, the heat of combustion may be theoretically determined by the formula,

$$Q = 7050\,\mathrm{C} + 34{,}500 \left(\mathrm{H} - \frac{0}{8}\right) - 650\ \mathrm{H_2O}, \text{ in calories, or}$$

$$= 12{,}690\,\mathrm{C} + 62{,}100 \left(\mathrm{H} - \frac{0}{8}\right) - 1170\ \mathrm{H_2O}, \text{ in British}$$

thermal units.

This equation can be only approximate, because no account is made of the positive or negative heat of formation of the product under consideration.

The amounts of heat noted above were determined in a calorimeter in which the products of combustion were reduced to the surrounding temperature. In many cases this is sufficient. But when it is desired to find the maximum amount of work that can be obtained from an ideal explosion engine, measured by the ratio $\frac{Q_0 - Q_1,}{Q_0}$ where Q_0 represents the maximum heat developed, Q_1 the heat given up and not transformed into work, it is necessary to know the difference, $Q_0 - Q_1$.

Q_1 is composed of two parts, one constant, which is the heat of vaporization carried away by the water vapor, the other variable with the amount of air introduced, but which may be easily calculated from a table giving the specific heat of the gases oxygen and nitrogen.

The following table gives the heats of combustion in calories corrected for the quantity corresponding to the water vapor present, and to the products of theoretical combustion on the supposition that these products are rejected at temperatures of 100° C, 200° C, 300° C, 400° C, and 500° C.

Substance.	Final Temperature of Products of Combustion in Degrees Centigrade.				
	100°	200°	300°	400°	500°
Hydrogen	23,650	23,222	22,761	22,268	21,746
Amorphous carbon	8,011	7,933	7,849	7,759	7,663
Carbon monoxide	2,400	2,367	2,331	2,293	2,252
Acetylene	11,717	11,612	11,499	11,378	11,248
Ethylene	11,311	11,185	11,049	10,903	10,748
Ethane	11,752	11,604	11,445	11,274	11,092
Methane	12,020	11,833	11,675	11,504	11,323
Allylene	11,021	10,903	10,781	10,651	10,510
Propylene	11,195	11,067	10,829	10,681	10,522
Propane	11,479	11,336	11,183	11,020	10,846
Amylene	10,607	10,479	10,331	10,183	10,024
Benzene	9,440	9,335	9,222	9,101	8,882
Naphthalene	9,280	9,180	9,072	8,958	8,836
Methyl alcohol	4,567	4,484	4,395	4,300	4,198
Ethyl alcohol	6,282	6,201	6,114	6,021	5,921
Acetone	6,771	6,679	6,579	6,472	6,358
Aldehyde	5,564	5,483	3,395	5,301	6,201
90% methyl alcohol	3,837	3,757	3,671	3,579	3,471
90% ethyl alcohol	5,295	5,219	5,137	5,050	4,961
Mixture of 10 volumes of 90% ethyl alcohol and 1 volume of 90% methyl alcohol	5,171	5,095	5,014	4,935	4,841
Mixture of equal parts of alcohol and benzene	7,391	7,307	7,196	7,090	6,937

As has been said, it is still necessary to subtract from these numbers the heat carried away by the excess of air. In the case of a four cycle motor, it should be noted that the exhaust takes place at constant pressure and the combustion at constant volume. Hence, it is necessary to add to the preceding numbers the positive or negative difference between the heats of combustion at constant pressure and at constant volume.

Finally, as will appear later, in numerous cases in practice, combustion is far from complete; if the analysis of the exhaust gases shows the presence of unburned constituents, it is necessary to diminish these theoretic numbers by the quantity of heat that would have been furnished by the combustion of these constituents.

Specific heat of the products of combustion. — As with the heat of combustion, it is necessary to use, as the case may be, either the specific heat at constant volume or at constant pressure. There is a decided difference between these two specific heats. This difference corresponds to the production of external work under the pressure, P, equal to $APdV$. Hence, the relation between the specific heats is given by the equation:

$$C_p\, dT = C_v\, d\,T + APdV.$$

As we have seen, $APV = 2\,T$, approximately.

Hence, $APdV = 2\,dT.$

or, $C_p = C_v + 2$

in which C_p and C_v represent the molecular specific heats.

The ratio between the two specific heats is not constant but varies with the molecular weights of the bodies considered.

Regnault gave the following values:

SPECIFIC HEATS COMPARED WITH WATER AS UNITY.

	At Constant Pressure c_p.	At Constant Volume c_v.	$\frac{c_p}{c_v}$
Nitrogen	0.2440	0.1717	1.421
Hydrogen	3.4046	2.3910	1.423
Oxygen	0.2182	0.1547	1.410
Air	0.2370	0.1668	1.421
Carbon monoxide	0.2479	0.1753	1.429
Carbon dioxide	0.2164	0.1702	1.241
Water vapor	0.4750	0.3621	1.312

These values were supposed to be accurate up to 900° C. (1650° F.)

More recent investigations show that specific heats are linear functions of temperature.

Mallard and Le Chatelier (*Annales des Mines*, 1883: *Mémoires*, vol. iv, page 510) have given the following approximate values for those substances which interest us especially as forming the products of combustion; c_v and c_p represent the ordinary specific heats at constant volume and constant pressure, respectively, compared with water as unity; t represents the temperature on the ordinary centigrade scale, and T the absolute temperature on the centigrade scale:

Carbon dioxide . . $\begin{cases} c_v = 0.143 + 0.000167t = 0.097 + 0.000167T \\ c_p = 0.188 + 0.000167t = 0.142 + 0.000167T \end{cases}$

Water vapor . . . $\begin{cases} c_v = 0.312 + 0.000364t = 0.213 + 0.000364T \\ c_p = 0.421 + 0.000364t = 0.322 + 0.003364T \end{cases}$

Nitrogen . . . . . $\begin{cases} c_v = 0.171 + 0.000043t = 0.159 + 0.000043T \\ c_p = 0.241 + 0.000043t = 0.229 + 0.000043T \end{cases}$

Oxygen . . . . . $\begin{cases} c_v = 0.150 + 0.000038t = 0.140 + 0.000038T \\ c_p = 0.211 + 0.000038t = 0.201 + 0.000038T \end{cases}$

Air . . . . . $\begin{cases} c_v = 0.166 + 0.000042t = 0.155 + 0.000042T \\ c_p = 0.234 + 0.000042t = 0.213 + 0.000042T \end{cases}$

Berthelot and Vieille (*Comptes Rendus*, 1884, vol. xcviii, page 852) published the following results, in which C_v and C_p represent the molecular specific heats,

that is the ordinary specific heats multiplied by the molecular weight of the substance concerned, and the other letters have the same meanings as before.

Temperatures Above 2000° C.

Carbon Dioxide.

$c_v = 0.434 + 0.000068\,(t - 2000)$ $\quad C_v = 19.1 + 0.00299\,(t - 2000)$
$c_p = 0.480 + 0.000068\,(t - 2000)$ $\quad C_p = 21.1 + 0.00299\,(t - 2000)$

Water Vapor.

$c_v = 0.900 + 0.000211\,(t - 2000)$ $\quad C_v = 17.1 + 0.00380\,(t - 2000)$
$c_p = 1.011 + 0.000211\,(t - 2000)$ $\quad C_p = 19.1 + 0.00380\,(t - 2000)$

Temperatures from 1600° to 2000° C.

Nitrogen.

$c_v = 0.170 + 0.000144\,(t - 1600)$ $\quad C_v = 4.76 + 0.00319\,(t - 1600)$
$c_p = 0.242 + 0.000144\,(t - 1600)$ $\quad C_p = 6.76 + 0.00319\,(t - 1600)$

Oxygen.

$c_v = 0.149 + 0.000100\,(t - 1600)$ $\quad C_v = 2.38 + 0.00160\,(t - 1600)$
$c_p = 0.211 + 0.000100\,(t - 1600)$ $\quad C_p = 4.38 + 0.00160\,(t - 1600)$

Air.

$c_v = 0.165 + 0.000111\,(t - 1600)$ $\quad C_v = 4.22 + 0.00284\,(t - 1600)$
$c_p = 0.235 + 0.000111\,(t - 1600)$ $\quad C_p = 6.22 + 0.00284\,(t - 1606)$

Temperatures from 2000° to 4000° C.

Nitrogen.

$c_v = 0.239 + 0.000114\,(t - 2000)$ $\quad C_v = 6.69 + 0.00319\,(t - 2000)$
$c_p = 0.311 + 0.000114\,(t - 2000)$ $\quad C_p = 8.69 + 0.00319\,(t - 2000)$

Oxygen.

$c_v = 0.209 + 0.000100\,(t - 2000)$ $\quad C_v = 3.34 + 0.00160\,(t - 2000)$
$c_p = 0.272 + 0.000100\,(t - 2000)$ $\quad C_p = 5.34 + 0.00160\,(t - 2000)$

Air.

$c_v = 0.232 + 0.000111\,(t - 2000)$ $\quad C_v = 5.93 + 0.00284\,(t - 2000)$
$c_p = 0.302 + 0.000111\,(t - 2000)$ $\quad C_p = 7.93 + 0.00284\,(t - 2000)$

Calorimetric experiments made at temperatures so high are exceedingly difficult to perform with exactness. Naturally, considerable discrepancies may be expected in the two sets of figures. The following table gives the values of c_v, the specific heat at constant volume compared with water, as obtained at a temperature of 2000° C. (3600° F.), by the above experimenters.

SPECIFIC HEAT AT CONSTANT VOLUME, c_v.

	Mallard and Le Chatelier	Berthelot and Vieille
Carbon dioxide	0.477	0.434
Water vapor	1.040	0.900
Nitrogen	0.259	0.216
Oxygen	0.226	0.189
Air	0.250	0.209

The results of Mallard and Le Chatelier have been sharply criticised by some scientists. Perhaps their values are too large. Nevertheless, until better values are available, they may be used up to 2000° C. (3600° F.) beyond which the figures given by Berthelot and Vieille may be used.

Temperature of combustion. — To calculate theoretically the heat produced and the temperature reached by a complete reaction, the conditions following the combustion must be taken into account. The following table is based on the supposition that the whole of each substance is burned, that the products of combustion remain in the gaseous state just as they are formed at the moment of explosion, and that the quantity of air present is only the amount strictly necessary for the combustion.

Substances.	Molecular weights.	Products of Combustion Corresponding to 1 lb. or to 1 Kilogram.		
		CO_2	H_2O	N
		lbs. or kg.	lbs. or kg.	lbs. or kg.
H_2	2	0.000	9.000	26.666
CO	28	1.571	. . .	1.911
METHANE SERIES, C_nH_{2n+2}.				
CH_4	16	1.735	2.025	13.378
C_2H_6	30	2.932	1.800	12.863
C_3H_8	44	2.995	1.638	12.171
C_4H_{10}	58	3.032	1.557	12.043
C_5H_{12}	72	3.054	1.503	11.999
C_6H_{14}	86	3.069	1.467	11.825
C_7H_{16}	100	3.080	1.440	11.772
C_8H_{18}	114	3.085	1.423	11.736
C_9H_{20}	128	3.090	1.406	11.706
$C_{10}H_{22}$	142	3.098	1.395	11.684
ETHYLENE SERIES, C_nH_{2n}.				
C_2H_4	28	3.142	1.287	7.582
C_3H_6	42	"	"	"
C_4H_8	56	"	"	"
C_5H_{10}	70	"	"	"
ACETYLENE SERIES, C_nH_{2n-2}.				
C_2H_2	26	3.384	0.693	8.233
C_3H_4	40	3.307	0.900	8.028
C_4H_6	54	3.259	0.999	7.931
BENZENE SERIES, C_nH_{2n-6}.				
C_6H_6	78	3.384	0.693	8.233
C_7H_8	92	3.347	0.783	8.114
C_8H_{10}	106	3.318	0.855	8.073
ALCOHOL AND DERIVATIVES.				
CH_4O	32	1.375	1.080	5.017
C_2H_6O	46	1.900	1.117	6.982
C_3H_6O	582	2.224	0.931	7.834

The use of the preceding tables is illustrated in the following examples:

To calculate the temperature of combustion of hydrogen and air at constant pressure. By the table on page 71, the combustion of one kilogram of hydrogen produces 29,100 calories, which is distributed between the products of combustion, which are, according to the table on page 78, 9 kilograms of water and 26,666 kilograms of nitrogen.

Let us assume in all the following calculations that the initial temperature is 0° C.

Using the specific heats from the table on page 75, the temperature of combustion under constant pressure will be determined by the equation:

$$\int_0^t 9\,(0.421 + 0.000364t)dt +$$

$$\int_0^t 26.666\,(0.241 + 0.000043t)dt = 29{,}100.$$

Whence, $t = 2111°$ C.

Under ordinary pressure this temperature cannot be reached because dissociation would prevent complete combustion.

To calculate the temperature of combustion of carbon monoxide in a closed vessel:

One kilogram of carbon monoxide burned at constant volume yields 2425 calories, and the products of combustion consist of 1.571 kilograms of carbon dioxide and 1.911 kilograms of nitrogen. To heat the mixture of the products of combustion from 0° to 2000° requires:

$$\int_0^{2000} 1.571\,(0.143 + 0.000167t)dt +$$

$$\int_0^{2000} 1.911(0.171 + 0.000043t)dt \text{ or } 1792 \text{ calories.}$$

Hence there remain available 633 calories to heat the mixture above 2000°.

If t is the final temperature,

$$\int_{2000}^{t} 1.571 \ (0.298 + 0.00068t)dt +$$

$$\int_{2000}^{t} 1.911 \ (0.311 + 0.000114t)dt = 633.$$

Whence, $t = 2427°$ C.

It is probable that dissociation would prevent the reaching of this temperature.

Hexane, $C_6 H_{14}$, which may be considered the principal compound contained in gasoline as used in engines, has a molecular weight of 86. Hence its vapor has theoretically a density of 3.853 kilograms per cubic meter. Then, according to Staby's rule, 3.853 kilograms would produce by its combustion in a state of vapor,

$$1000 + 10{,}500 \times 3.853 = 41{,}456 \text{ calories.}$$

Therefore, 1 kilogram of hexane vapor produces 10,760 calories. Its combustion with only the theoretically necessary amount of air yields as products of the combustion, 3.069 kilograms of CO_2, 1.467 kilograms of H_2O, and 11.825 kilograms of nitrogen. Whence the temperature of combustion of 2290° C is found.

But if to assure complete combustion, it is assumed that one and one half times the theoretical quantity of air must be introduced, 7.685 kilograms of air must be heated up in addition to the previously considered products of combustion and the temperature of combustion will fall to 1869° C.

With the same amount of excess air, the French denatured alcohol would give the almost identical temperature, 1871° C, and the same alcohol mixed with an equal volume of benzene would develop a temperature of 2033° C.

For simplicity we have supposed the initial temperature to be 0° C. In fact, especially in high speed engines, the

temperature of combustion must be much higher, for the gases enter hot and are further heated by the high compression.

In slow speed engines, there is a slight counteraction due to the cooling effect of the cylinder walls during the very short time of combustion.

Moreover, the combustion has to warm up the burned gases remaining from the preceding explosion, partially cooled in the meantime by the work of expansion and by contact with the surrounding walls.

Lastly, while we have assumed the combustion to be complete, we shall find that in practice it is rarely so.

However, the figures given above are not very far from the truth, for in many engines the temperature is high enough to melt very fine platinum wire.

Explosive power. — The substitution of one fuel for another in the same engine shows that under identical conditions some fuels produce violent hammering that is scarcely perceptible with other fuels. This hammering causes a deterioration of the engine and a loss of efficiency and hence it is not to be ignored.

As shown before, increase of temperature and pressure may change a non-explosive reaction to an explosive reaction. The boundary between the two types of reaction varies greatly with different fuels. This accounts for the variation in hammering mentioned above.

Moreover, there must be considered the sudden increase of volume produced by the explosion. The amount of this depends upon two things: the sudden increase of temperature and the variation in volume, at constant temperature, due to the change of the combustible into water vapor and carbon dioxide. The latter variation may be either positive or negative, all the steam being supposed to remain in the vapor state.

For mixtures of various substances with exactly the quantity of oxygen necessary for their complete combustion, the following table shows the volume of the products of combustion corresponding to one volume of the explosive mixture:

Hydrogen	0.667
Carbon monoxide	0.667
Methane Series.	
Methane, CH_4	1.000
Ethane, C_2H_6	1.111
Propane, C_3H_8	1.167
Butane, C_4H_{10}	1.200
Pentane, C_5H_{12}	1.220
Hexane, C_6H_{14}	1.238
Heptane, C_7H_{16}	1.250
Octane, C_8H_{18}	1.259
Nonane, C_9H_{10}	1.267
Decane, $C_{10}H_{22}$	1.273
Ethylene Series.	
Ethylene, C_2H_4	1.000
Propylene, C_3H_6	1.090
Butylene, C_4H_8	1.143
Amylene, C_5H_{10}	1.176
Acetylene Series.	
Acetylene, C_2H_2	0.857
Allylene, C_3H_4	1.000
Benzene Series.	
Benzene, C_6H_6	1.059
Toluene, C_7H_8	1.100
Xylene, C_8H_{10}	1.130
Alcohol and Derivatives.	
Methyl alcohol, CH_4O	1.200
Ethyl alcohol, C_2H_6O	1.250
Acetone, C_3H_6O	1.200
90 per cent methyl alcohol	1.179
90 per cent ethyl alcohol	1.256
Denatured alcohol	1.220

Maximum Pressure. — Assuming there is no cooling, the maximum pressure in an engine may be calculated. Assume as before that the specific heat is a linear function of temperature.

$$c_v = c + sT$$
$$c_p = Kc + sT.$$

If the compression stroke is adiabatic,

$$c_v vdp + c_p pdv = 0$$

or

$$(c + sT)\, vdp + (Kc + sT)\, pdv = 0$$

$$c(vdp + Kpdv) + sTd(pv) = 0 \qquad (1)$$

The equation of a perfect gas is

$$pv = RT, \qquad (2)$$

in which the value of $R^* = \frac{c_p - c_v}{A} = \frac{c(K-1)}{A}$, where A = the reciprocal of the mechanical equivalent of heat.

Dividing equation (1) by (2) we get

$$\frac{c(vdp + Kpdv)}{pv} + \frac{s}{R}\,d(pv) = 0.$$

Multiplying both terms of the first fraction by v^{k-1},

$$\frac{c(v^k dp + Kpv^{k-1}dv)}{pv^k} + \frac{s}{R}\,d(pv) = 0.$$

Integrating,

$$\text{natural log } pv^k + \frac{s}{cR}\,pv = \text{a constant.}$$

Supposing the volume of the compression chamber to be one quarter of the whole cylinder, using air as the gas to be experimented with, the pressure obtained in the compression chamber will be given by the equation:

$$\text{natural lop } p_1v_1^{1.44} + 0.00000925\,p_1v_1 =$$
$$\text{natural log } p_2v_2^{1.44} + 0.00000925\,p_2v_2.$$

Whence,

$$\text{natural log}\left[\frac{p_2}{p_1}\left(\frac{v_2}{v_1}\right)^{1.44}\right] = -\,0.00000925\,p_1v_1\left(\frac{p_2v_2}{p_1v_1} - 1\right).$$

If p_1 and v_1 be taken as unity,

$$\text{natural log } p_2 = \text{natural log } 4^{1.44} - 0.00000925\left(\frac{p_2}{4} - 1\right),$$

which gives approximately for p_2 the value 7.

* Values of R are as follows in metric units :

Carbon dioxide	19.23
Water	46.89
Nitrogen	26.99
Oxygen	26.12
Air	28.97

If the air has been previously heated to 50°, so that $T_1 = 273 + 50 = 323°$, then from the relation

$$\frac{p_2 v_2}{p_1 v_1} = \frac{T_2}{T_1}, \text{ we obtain } T_2 = 565°.$$

The explosion produced at constant volume causes a rise of temperature, D, the method of calculation for which has been indicated on page 79. The final temperature, T_3, equals $T_2 + D$. Hence,

$$\frac{p_3}{p_2} = \frac{T_3}{T_2} = 1 + \frac{D}{T_2}.$$

Therefore, the greater the initial compression, the higher will be the maximum pressure; but the latter is not proportional to the former, since the term $\frac{D}{T}$ diminishes as the compression increases.

In what precedes, it is supposed that there is no variation in volume due to the chemical change during combustion. Evidently, in general, it is necessary to take into account this variation, by substituting $p_2\ (1 + f)$ for the value p_2 in the last equation. The value of f may be either positive or negative and must be calculated in each case according to the nature of the combustible and the excess of air and of the products of previous combustion present. If this excess is considerable, the value of f may be neglected.

CHAPTER V.

ACTUAL COMBUSTION IN ENGINES.

Thermal efficiency of engines. — Often to form an idea of the possible efficiency of a combustible in an engine, all the secondary causes likely to bear on this efficiency are considered, and impossible assumptions are made concerning them.

Among these assumptions are:

1. That at the end of the compression stroke the ignition of the gas is instantaneous, and that there is no loss of heat. 2. That at the moment of opening the exhaust valve, the decrease of pressure is equally instantaneous. 3. That the new supply of explosive mixture is admitted without loss of pressure. 4. That the work of compression and the work of expansion take place according to two adiabatic curves answering to the equation $pv^k = C$.

If these assumptions were true, the cycle of an explosion engine would be represented by two vertical lines contained between two adiabatic curves answering to the above equation, and the thermal efficiency would be represented by the ratio $\frac{Q_0 - Q_1}{Q_0}$, in which Q_0 is the heat due to combustion and Q_1 the heat given up to the cold body, that is to say, carried away by the exhaust gases.

On pages 71 and 73, the values of Q_0 and $Q_0 - Q_1$ have been given; the latter correspond to different temperatures of the exhaust gases, on the supposition that air has been admitted in the proportion theoretically necessary for combustion, and that the combustion has been complete.

If this simple reaction were true, then with benzene burned with the theoretical mixture of air, Q_0 would equal 9985 and $Q_0 - Q_1$ would equal 8882, for a temperature of the exhaust gases of 500° C; consequently the thermal efficiency would be

$$\frac{8882}{9985} = 88.95 \text{ per cent.}$$

Under the same conditions, for a mixture of 90 per cent ethyl and methyl alcohols, mixed in the proportion of ten volumes of ethyl and one of methyl, Q_0 would equal 5923 and $Q_0 - Q_1$ would equal 4881. Hence the thermal efficiency would be

$$\frac{4881}{5923} = 82.40 \text{ per cent.}$$

Such high values are in practice never realized. Many engines operated on gasoline do not give an efficiency higher than 14 per cent, although some very large engines driven by poor blast furnace gases give an efficiency of 30 to 33 per cent. It is rare with carburated alcohol to exceed 25 per cent, although some have attained 34 per cent.

The reasons for such great divergence must be sought.

Influence of the heat of combustion. — While according to the above calculations the heat of combustion has little effect on thermal efficiency, practically it is of great importance.

According to experiments on the heat of combustion made in a bomb calorimeter with French denatured alcohol, a calorific power of 5906 calories per kilogram has been found in place of the theoretical value of 5923, and with alcohol carburated with its own volume of benzene 7878 calories have been reached, or a ratio of 0.749 between the two heats of combustion.

At the competition in November, 1901, instituted by the French Department of Agriculture, the jury had occasion to try these two combustibles in eleven different engines, differing both in power and in type. The engines, carefully run by the exhibitors themselves, gave the following results, in which F represents the specific consumption of French denatured alcohol per horse power per hour, G, the specific consumption of carburated alcohol per horsepower per hour, and R = the ratio $\frac{G}{F}$.

Power of the Engines in Metric Horsepower.	Fuel Consumption per Metric Horsepower per Hour in Grams.		$R = \frac{G}{F}$
	Carburated Alcohol = G	Denatured Alcohol = F	
1.27 to 1.20	645	917	0.701
2.9 to 2.8	529	750	0.705
3.7 to 3.7	409	565	0.724
4.0 to 3.8	577	674	0.856
4.7 to 4.8	484	705	0.686
6.0 to 6.0	435	615	0.707
6.2 to 5.9	439	668	0.657
9.5 to 9.4	379	507	0.748
9.67 to 8.97	500	721	0.693
11.6 to 8.4	459	570	0.805
16.1 to 14.7	382	491	0.778
		Average	0.733

Great differences in the ratio might be expected, because it is evidently very difficult to regulate equally well an engine in the two consecutive trials. Nevertheless, from the study of a large number of engines a very satisfactory agreement appears between the practical ratio and the theoretical ratio of specific consumptions calculated according to the calorific powers.

The calculations of the jury of the international competition at Paris in May, 1902, confirmed the correctness of this ratio.

Incomplete combustion. Influence of the proportion of air. — A great cause of low efficiency is poor or incomplete combustion. During the French test of May, 1902, the author analyzed the exhaust gases of many stationary engines and examined the condition of the valves after their operation. The gas samples were taken through a little silver tube inserted as close as possible to the exhaust valve. The samples were immediately cooled in a metallic coil. Thus any condensed portion could be gathered in small amounts. When the coil was well freed of air an instantaneous sample was obtained by inserting into the coil the sealed point of a testing tube in which previously a vacuum had been produced. At the proper moment the point was broken and again sealed before separating the testing tube from the coil. The sample was taken while the motor was working at full load, and care was taken to wait a certain number of strokes after a miss in order that the combustion might be as perfect as possible.

By analysis, there were determined the free oxygen, the carbon dioxide, the carbon monoxide, the various gaseous hydrocarbons (consisting of the acetylene group, the methane group from methane to pentane, and sometimes a little benzene). Finally the residue of nitrogen enabled the original quantity of air to be calculated.

The details of these analyses were given in the *Rapport des Jurys du Concours international des moteurs et appareils employant l'alcool dénaturé ayant eu lieu à Paris, en Mai,* 1902. A summary only of the results is given here.

On the supposition that after the combustion all the carbon had combined in gaseous compounds (which is only true when black smoke is not observed), and that the results were not affected by the combustion or decomposition of an amount of lubricating oil, small in compari-

son with the consumption of the alcohol, the results were computed as follows:

The quantity of alcohol fuel burned in the cylinder was calculated from the total quantity of carbon found. The amount of carbon not utilized was ascertained from the quantity combined in other forms than carbon dioxide. From the quantity of hydrogen remaining in the form of hydrocarbons was found the amount of hydrogen not utilized and its ratio to the total amount of hydrogen.

The following table summarizes the results of these analyses. It follows the arrangement of the jury where the engines are classed, not only according to their power, but also according to their weight per useful horsepower and their speed.

The fuel used was either French denatured alcohol or that alcohol carburated by an equal volume of pure benzene.

It is seen on the one hand that generally more than the theoretical amount of air must be introduced to obtain an approximately perfect combustion; this increase of air augments the loss of heat removed by the burned gases; on the other hand that very few engines showed complete combustion, in spite of the care taken by their operators. Consequently the number of calories furnished is not what is calculated from the amount of fuel consumed; in fact the actual amount may fall far short of the theoretical amount. From this fact comes, in a great degree, the vast difference found in the consumption per horsepower per hour in engines with like power.

RESULTS OF FRENCH TESTS OF MAY, 1902.

Number.	Weight of Engine in Kilograms.	Power in Metric Horse-power by Test.	Revolutions per Minute.	Kind of Alcohol Fuel Used.	Amount of Load.	Fuel Consumed.		Ratios.		
						Kilograms per Hour.	Kilograms per Hour per Metric Horse-power.	Air Introduced to Air Necessary.	Carbon not Utilized to Total Carbon.	Hydrogen not Utilized to total Hydrogen.
								Per Cent.	*Per Cent.*	*Per Cent.*
			282.3	Carburated	No load	0.426				
2	535	0.955	305.1	"	Half "	0.526	0.551			
		1.83	292.6	"	Full "	1.010	0.551	1.44	8.93	10.00
								1.69	6.62	6.26
			243.2	Denatured	No load	0.812				
3	450	0.923	251	"	Half "	1.100	1.192			
		1.866	246	"	Full "	1.470	0.788	2.26	24.84	23.10
			455.3	Carburated	No load	0.506				
4	220	0.691	429.3	"	Half "	0.930	1.345			
		1.038	432.0	"	Full "	1.060	1.020	0.87	45.16	84.16
			1127.0	Carburated	No load	1.083				
6	90	3.061	1154.0	"	Half "	1.512	0.494			
		6.144	1158.0	"	Full "	2.376	0.387	1.75	38.94	44.37
			257.5	Carburated	No load	0.746				
7	505	1.814	248.2	"	Half "	1.714	0.945			
		3.189	244.3	"	Full "	2.011	0.631	1.59	7.11	4.38

Number.	Weight of Engine in Kilograms.	Power in Metric Horse-power by Test.	Revolutions per Minute.	Kind of Alcohol Fuel Used.	Amount of Load.	Fuel Consumed.		Ratios.		
						Kilograms per Hour.	Kilograms per Hour per Metric Horse-power.	Air Introduced to Air Necessary.	Carbon not Utilized to Total Carbon.	Hydrogen not Utilized to Total Hydrogen.
								Per Cent.	*Per Cent.*	*Per Cent.*
			265.0	Carburated	No load	0.790				
9	857	3.521	257.3	"	Half "	1.824	0.519			
		5.95	247.0	"	Full "	2.792	0.469	1.86	29.0	43.1
			265.0	Carburated	No load	1.048				
11	900	2.41	259.3	"	Half "	2.170	0.900			
		4.54	254.1	"	Full "	2.654	0.584	1.28	8.68	14.68
			253.0	Carburated	No load	0.327				
12	1200	3.246	244.0	"	Half "	1.295	0.399			
		5.150	239.2	"	Full "	1.680	0.326	1.47	6.92	0.0
		5.050	238.0	Denatured	Full "	2.423	0.479			
			845.0	Carburated	No load	1.794				
14	150	5.203	790.5	"	Half "	3.764	0.727			
		10.61	761.7	"	Full "	6.191	0.583	0.81	13.08	137.57
			966.0	Carburated	No load	2.316				
15	130	3.700	983.0	"	Half "	2.568	0.694			
		7.11	927.0	"	Full "	3.374	0.474	2.14	38.98	21.76

RESULTS OF FRENCH TESTS OF MAY, 1902.—*Continued.*

Number.	Weight of Engine in Kilograms.	Power in Metric Horse-power by Test.	Revolutions per Minute.	Kind of Alcohol Fuel Used.	Amount of Load.	Fuel Consumed.		Ratios.		
						Kilograms per Hour.	Kilograms per Hour per Metric Horse-power.	Air Introduced to Air Necessary.	Carbon not Utilized to Total Carbon.	Hydrogen not Utilized to Total Hydrogen.
								Per Cent.	*Per Cent.*	*Per Cent.*
			250.0	Carburated	No load	1.338				
18	1200	3.426	245.5	"	Half "	2.554	0.745			
		6.46	240.0	"	Full "	3.458	0.535	1.54	52.40	84.01
			187.0	Carburated	No load	0.644				
		4.630	185.0	"	Half "	1.830	0.395			
19	1400	8.351	184.2	"	Full "	2.820	0.337			
		7.98	185.0	Denatured	Full "	3.516	0.440	1.52		0.0
			317.3	Carburated	No load	1.004				
20	1000	3.752	309.8	"	Half "	2.476	0.660			
		7.201	300.8	"	Full "	4.786	0.665	0.88	42.74	52.43
			269.2	Denatured	No load	0.880				
21	800	4.802	268.0	"	Half "	2.778	0.578			
		9.021	259.7	"	Full "	6.088	0.675	1.18	33.33	49.94

Number.	Weight of Engine in Kilograms.	Power in Metric Horse-power by Test.	Revolutions per Minute.	Kind of Alcohol Fuel Used.	Amount of Load.	Fuel Consumed.		Ratios.		
						Kilograms per Hour.	Kilograms per Hour per Metric Horse-power.	Air Introduced to Air Necessary.	Carbon not Utilized to Total Carbon.	Hydrogen not Utilized to Total Hydrogen.
								Per Cent.	*Per Cent.*	*Per Cent.*
			1009.0	Carburated	No load	1.430				
22	170	6.297	1061.0	"	Half "	2.406	0.382			
		10.69	1134.0	"	Full "	4.248	0.398	1.13	42.08	82.4
			1300.7	Carburated	No load	2.362				
23	130	8.869	1337.3	"	Half "	3.850	0.434			
		15.817	1294.7	"	Full "	7.020	0.444	1.90	95.00	17.14
			204.7	Carburated	No load	0.598				
25	2615	8.768	208.3	"	Half "	2.698	0.308	1.41	14.7	3.09
		16.337	198.7	"	Full "	3.810	0.233	1.45	0.0	0.0
		12.714	183.5	Denatured	Full "	4.32	0.340	1.27	0.0	0.0
			226.4	Denatured	No load	1.476				
26	1600	6.101	223.2	"	Half "	3.746	0.614			
		12.179	220.0	"	Full "	6.346	0.521	1.05	20.21	8.78

RESULTS OF FRENCH TESTS OF MAY, 1902.—*Continued.*

Number.	Weight of Engine in Kilograms.	Power in Metric Horse-power by Test.	Revolutions per Minute.	Kind of Alcohol Fuel Used.	Amount of Load.	Fuel Consumed.		Ratios.		
						Kilograms per Hour.	Kilograms per Hour per Metric Horse-power.	Air Introduced to Air Necessary.	Carbon not Utilized to Total Carbon.	Hydrogen not Utilized to Total Hydrogen.
								Per Cent.	*Per Cent.*	*Per Cent.*
			200.2	Carburated	No load	2.226				
		7.09	194.5	"	Half "	4.029	0.568			
27	2000	14.02	191.0	"	Full "	5.925	0.423	1.30	11.46	3.09
								1.62	0.0	0.0
		10.59	181.3	Denatured	Full "	6.038	0.570	1.33	13.35	0.0
								1.26	12.53	4.23
			225.7	Denatured	No load	1.636				
		7.82	228.8	"	Half "	3.712	0.474			
28	2400	11.70	210.3	"	Full "	7.856	0.671	1.04	4.61	4.18
								0.97	43.47	76.34
		11.21	214.0	Carburated	Full "	3.863	0.345	1.09	5.02	0.0
								1.000	23.82	41.97
			211.6	Carburated	No load	2.288				
31	6300	17.56	207.0	"	Half "	6.406	0.370			
		34.37	203.8	"	Full "	10.074	0.293	1.83	16.44	0.0
		34.46	204.4	Denatured	Full "	13.268	0.385	1.72	1.5	2.38

The following diagram (Fig. 3) shows some results of the analyses summed up in the last columns. The ratio of the actual amount of the air compared with the theoretical amount is taken as the abscissa, the per cents of carbon and of hydrogen unused are taken as the ordinates; the black circles represent carbon, the white ones hydrogen. It is seen that the consumption becomes more perfect according as the ratio of the oxygen introduced to the oxygen necessary is increased to a certain limit, and that the effect for the same per cent of oxygen becomes less as the speed of the engine becomes greater.

If, giving a like weight to all the circles of the same kind, a curve is drawn passing through the centers of gravity of the circles having the same ordinate, the continuous curved line representing carbon and the crosses representing hydrogen, an idea may be had of the probable amount of the two elements unconsumed, according as the amount of oxygen used varies. It is seen that to burn hydrogen completely, probably in actual engines 1.33 times the theoretic quantity of air must be introduced; to burn carbon from 1.5 to 1.7 the theoretic quantity of air will be required. It will be seen later that according to the method of carbureting used, a cylinder may be furnished with homogeneous mixtures burning completely, or with imperfect mixtures, which even after compression may be composed of portions too rich in oxygen and other portions too poor.

Finally, an examination of the admission valve shows that in some engines the exterior surface remains very clean, while in others it is covered with tar products, or with lamp black or even coke. Consequently, even before admission to the cylinder, the combustible liquids may, according to the circumstances, even outside the cylinder, undergo partial oxidation from the action of the heat and

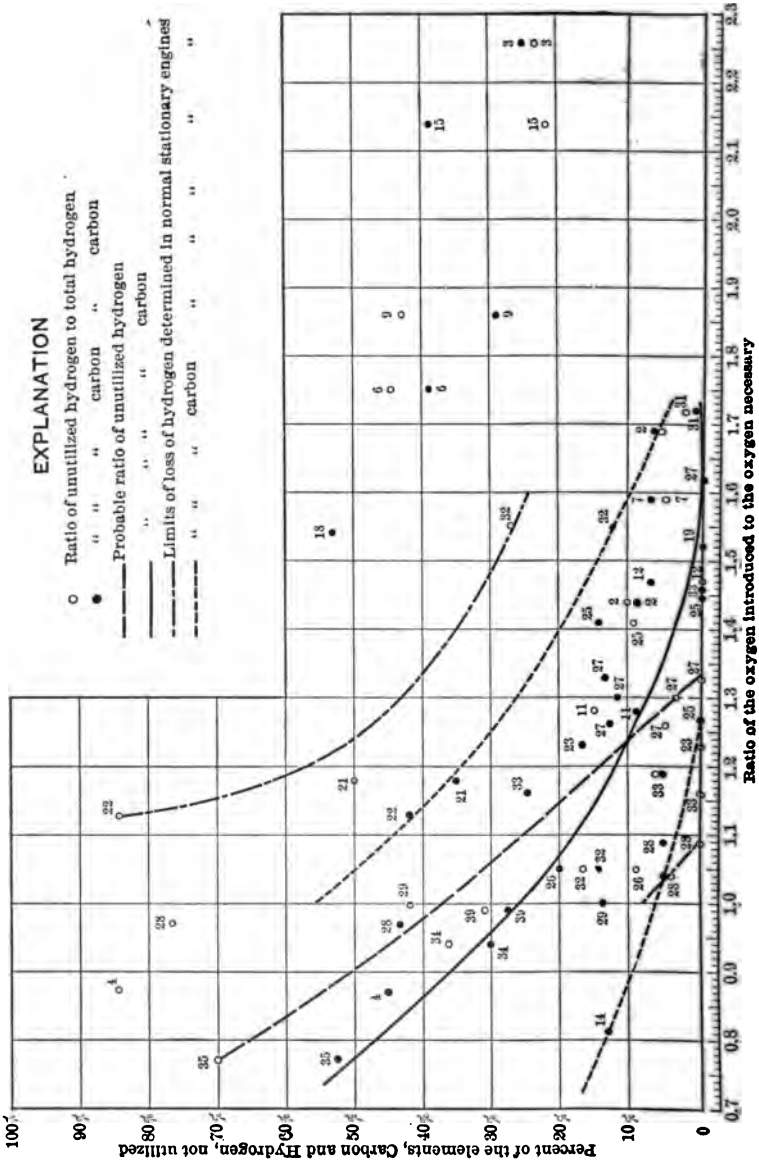

EXPLANATION
Ratio of unutilized hydrogen to total hydrogen
" " " carbon " carbon
Probable ratio of unutilized hydrogen
" " " carbon
Limits of loss of hydrogen determined in normal stationary engines
" " " carbon " " " "
Percent of the elements, Carbon and Hydrogen, not utilized
Ratio of the oxygen introduced to the oxygen necessary

FIG. 3.

the metallic walls, and thus lose a part of their calorific power.

In the above experiments the power was measured by a brake. It may differ considerably from the power the indicator diagram would show, in consequence of the more or less frictional resistance resulting from the mode of construction.

From the numerous analyses mentioned above it appears, contrary to the opinion of Witz, that engines with very great speed have efficiencies inferior to those of slow engines having the same power, a fact that harmonizes with the imperfect combustion observed.

Influence of cooling the walls. — It has been seen before that a water jacket must be used to permit lubrication and prevent pre-ignitions. Even if the water in this jacket is kept at its highest possible temperature a very active exchange of heat takes place through the thin walls of the cylinder and often from 40 to 50 per cent of the heat produced passes into the water. At the end of the expansion stroke, cooling is advantageous, because it lowers the final temperature, and consequently the heat given up to the cold body, which may be air or water. Cooling is harmful during the compression stroke, the explosion, and the first moments of expansion, since during these portions of the cycle cooling greatly diminishes the useful pressure against the piston during the expansion stroke which follows the explosion. This cooling is the more important as the temperature of the explosion is greater. This is the reason why engines using poor gases are superior in efficiency to engines for rich gases.

It must be noticed, besides, that engines for gas or liquid fuel are not so elastic as the variable expansion steam engines. Their efficiency is highest when the resistance to be overcome is approximately equal to the max-

imum power of the engine. It is usual to employ an engine a little more powerful than necessary, when working at full load, and to diminish the amount of work generated in one of the following ways, by the use of a governor:

1. By modifying the composition of the explosive mixture. This method gives rise to very poor combustion through excess of air. 2. By re-introducing the consumed gases, in this case, too, there is poor combustion through lack of air. 3. By cutting off all introduction of fuel until the engine has returned to its normal speed and automatically reëstablished the normal flow of fuel. This last case, known as governing on the hit-and-miss principle, is the one most employed.

In this case there are series of misses, shorter as the governing is more perfect, separated by a series of explosions, each of which should give the maximum work compatible with the conditions of operation of the engine.

Since there is no change in the cooling water circulation, there is a cooling of the cylinder corresponding to each miss, which causes during the next explosion a lessening of the useful work, and hence a loss of efficiency.

It may even happen that the combustion commences with a non-explosive combination, and only becomes explosive after a greater or less part of the fuel has burned and when the piston has moved through a considerable part of its stroke. These two causes lower considerably the maximum pressure.

Professor Schöttler (*Die Gazmachine*, 1902, page 329) describes, in this connection, some very interesting experiments which were made on a kerosene engine. After several misses of the engine he obtained the successive indicator diagrams shown superposed in Fig. 4. It is evident that in the first explosion the combustion is far from being instantaneous, and the diagram shows that

the useful work is greatly reduced. Then gradually the explosion becomes more sharp and the useful work is correspondingly increased.

When the cylinder walls were very much cooled, the combustion became slow and increased as the cylinder warmed up.

For these reasons, in the author's investigations upon the products of combustion in stationary engines, he adopted the rule of working upon the engine only under full load and of counting the number of explosions between

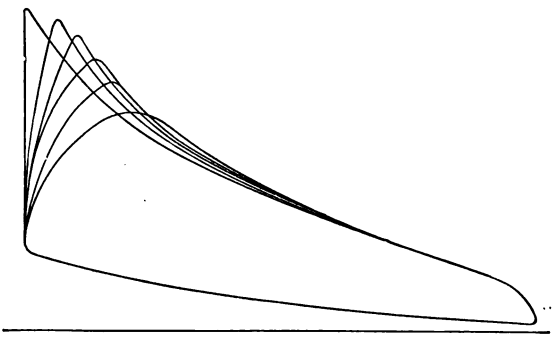


FIG. 4. — Indicator Diagrams from a Kerosene Engine after several Misses.

two misses, in order to take samples of the gases only when the cylinder was heated up.

Schöttler published the diagrams taken from the same engine and under the same load, but when the engine had made many consecutive explosions (Fig. 5). The diagrams were appreciably greater in area than those corresponding to the first explosion shown in Fig. 4, but the engine hammered. Hence, after a certain state there is a loss of work due to hammering.

When the engine hammers, the measurement of the area of the diagram becomes unreliable, because the upper

line of the figure becomes a series of waves. This uncertainty may be considerably diminished by the use of a powerful spring. But with the same indicator it is always found that the vibrations are greater as the load is greater and the number of misses is correspondingly fewer.

If the engine hammers, not only is the useful work diminished but the engine parts are liable to rapid wear. Generally smooth running and a satisfactory utilization of the fuel can be secured by diminishing the richness of the explosive mixture.

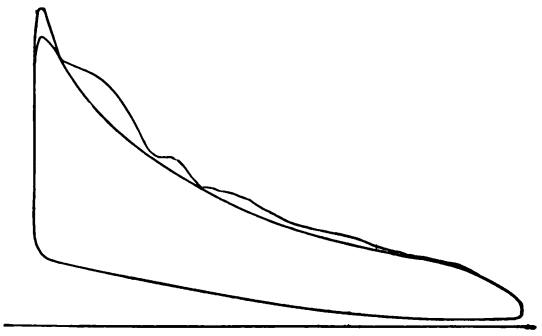


FIG. 5.—Diagrams from a Kerosene Engine when Overloaded.

Influence of time of ignition.—There is still another condition of efficiency to consider, that is the exact moment when the ignition of the explosive mixture takes place.

If there is too great increase of temperature, due to over compression or some other cause, self-ignition is produced before the end of the compression stroke. The preëxplosion is shown by a resistant work, and by hammering that at times is very great. The author has seen cases where the engine stopped even without load as a result of insufficient cooling of the cylinder. It is then allowable to say that the cooling of the cylinder is a necessary evil.

On the other hand, if the ignition does not take place till after the piston, under the influence of the fly wheel, has begun its return stroke, the explosion will produce on the piston only a part of its possible effect and the efficiency will be reduced.

An automobile engine of very small size, built to cool its cylinder by circulation of air, will cease to run if the engine is kept in motion a long time while the automobile is at rest, and will set free volumes of smoke.

An engine adjusted for a given fuel, and to given conditions of temperature and pressure might work well, and yet, with the composition of the fuel changed, it might happen that the total ignition did not take place at the exact moment when the piston was at the dead point, and consequently the efficiency might be considerably reduced. A skilful chauffeur will correct this defect by advancing the spark if ignition is caused by an electric spark; the problem will be almost impossible to solve where ignition is caused by an incandescent tube; in the latter case the only thing to do is to change the richness of the mixture or to experiment with tubes of various lengths.

The indicator diagram. — It is rare that the ignition and the total combustion are sudden; the ascending line of the diagram will not then be absolutely vertical, at least for very rapid motors; this seems clearly shown by the drawings of Hospitalier-Carpenter's monograph.

On the other hand, the expansion cannot be carried to its fullest extent. The exhaust valve must be opened before the gas has returned to its initial pressure. This is often done before the piston arrives at the dead point to diminish the back pressure in the cylinder.

Some force is lost during the suction, because the admission valve, generally automatic, does not open till a

certain vacuum is produced in the cylinder sufficient to overcome the resistance of the valve spring.

This is a question to which engine makers have given much thought. If the waves in the indicator diagram caused by the inertia of the indicator piston are neglected, the maximum point of the indicator diagram is far from reaching the maximum calculated on the supposition that the specific heat is constant, and yet in spite of the cooling the area of the diagram is often larger than that which will correspond to a diagram bounded by the adiabatic curves, pv^k = constant, assuming that these curves pass through the maximum and the minimum points of the drawing. Moreover, the curve of expansion is not the same for different fuels.

Several explanations of this result have been offered. It seems worth while to make a rapid criticism of them.

The case of French denatured alcohol demands special attention from the fact that its mean ordinates are much higher than those of the ordinary adiabatic curves and higher than those furnished by the Paris illuminating gas in an Otto engine.

An hypothesis, first proposed by Otto, depends upon the stratification of combustible mixtures. Otto thinks that a certain quantity of burned gases remains in the combustion chamber, and that, during the suction period, first some air and then a rich combustible mixture is added to it.

According to what will be seen later the order should be reversed. It is possible that such a heterogeneous gaseous mixture may not be sufficiently mixed in spite of the violent agitation the suction and the compression produce. Under these conditions, even if the ignition is communicated at exactly the right moment, the combustion would not be instantaneous, but a slow combustion would take place instead of an explosion. It has been seen from

Schöttler's experiments (p. 98), and from the studies made in the third chapter of this book, that the delay of explosion may be due to quite other causes.

Otto's hypothesis was accepted for a long time; it was even supposed that the slightly combustible mixture that was in contact with the piston played, up to a certain point, a favorable part by acting as a cushion to protect the engine against the effect of too violent hammering. This hypothesis seems to be abandoned to-day.

Wedding and Clerk give quite a different explanation, although also founded on the retardation of complete combustion. These authors suppose that the temperature produced in the combustion chamber is sufficient to cause the dissociation of the possible products. Consequently, there would be no longer instantaneous and complete combustion, but a partial combustion, becoming total only, when the mechanical work produced during the expansion, as well as contact with a very large cooling surface, had sufficiently absorbed the heat to reduce the unburned mixture to a temperature permitting a new partial combustion. The combination would not then be instantaneous, but would take place at successive intervals with an intensity decreasing in proportion as the unburned mass diminished in ratio to the inert gases. This hypothesis may be classed with the first experiments in which the use of too weak springs in the indicator produced distinct vibrations in the curve of expansion. But the use of better indicators has caused these vibrations to disappear and the idea of dissociation to be abandoned.

There remains to be discussed the influence of the cooling effect of the cylinder walls to which Witz attached a great deal of importance. The experiments of Schöttler, mentioned above, show that in certain cases the influence of cold walls causes slow combustion and consequently a

lowering of the highest point of the diagram, without raising the lower portion of the expansion curve an equivalent amount. But these experiments also show that this action has an important influence only when the cooling is extreme and under easily determined conditions. Under such conditions as during the starting of an engine, or when the cylinder is surrounded by a large quantity of cold water, or during trials without any load, an abundance of smoke indicates incomplete combustion. With denatured alcohol there is produced an abundance of formaldehyde whose injurious effects will be considered later.

According to the experiments made at the French competition of May, 1902, it seems that it is necessary to keep the jacket at the highest temperature compatible with the construction of the engine, but it does not seem to the author to be proved that it is necessary, as Witz thinks, to use weak mixtures and to operate at high speeds. It is probable that this scientist failed to take account of the composition of the burned gases, for if, on the one hand, a certain excess of air is necessary to produce perfect combustion in the engine studied, on the other hand, too great an excess causes a contrary result. Moreover, it has been seen in these experiments that the very high speed engines were the ones that showed the worst utilization of the fuel, and at the same time the poorest combustion.

It seems that the form of the expansion curve may be simply explained by giving up the assumption that the specific heat is constant and adopting the new values derived by Mallard and Le Chatelier and by Berthelot and Vieille. First of all it will be found that the temperature of combustion is much lower than was supposed. The maximum pressure is then lower. The adiabatic curve calculated under these conditions is less sharply curved and decreases less rapidly at the start than the curve

corresponding to the formula, pv^k = constant. Since the temperatures are lower the experimental expansion curve will approach more closely to the calculated curve.

Acidity of the exhaust gases. — During the tests of the French international competition in 1902, attention was called to the acidity of the exhaust gases, a thing raised as an objection to alcohol engines. Some acidity has always been noticed, but in quite variable amounts.

At one time it would be scarcely noticeable, at another it would be very great; moreover, at such times the combustion was incomplete.

The author is not prepared to say, as a result of his own experiments, that the acidity is proportional to the imperfect consumption of the alcohol, but until further information is found on the subject, it may be considered to vary in the same way.

In the above experiment the benzene was almost entirely free from thiophene; consequently this acidity would have to be attributed to incomplete combustion of the alcohol. This question will be taken up later. The bad effects of this acidity may be easily avoided by lubricating the engine with kerosene after it is shut down and while the engine is still hot.

Specific consumption. — If the figures derived from the experiments with stationary engines at the French international competition are examined, it will be seen that the specific consumption, that is to say, the consumption of the fuel per horsepower per hour varies greatly in different engines; but it is also seen that there are two kinds of variations; first, the specific consumption diminishes in a general fashion when the power increases; second, in engines of different types, having the same power, the consumption of fuel varies greatly.

If a drawing is made of the results obtained from the

tests at the French competition, taking for the abscissa, X, the brake horsepower, and for the ordinate, Y, the consumption of alcohol per hour (Fig. 6), and if for each engine the points, a, corresponding to operation at no load, n, to half load, and m, to full load, are joined, there are obtained two chords of the curve which represents the consumption of carburated alcohol at different loads; the

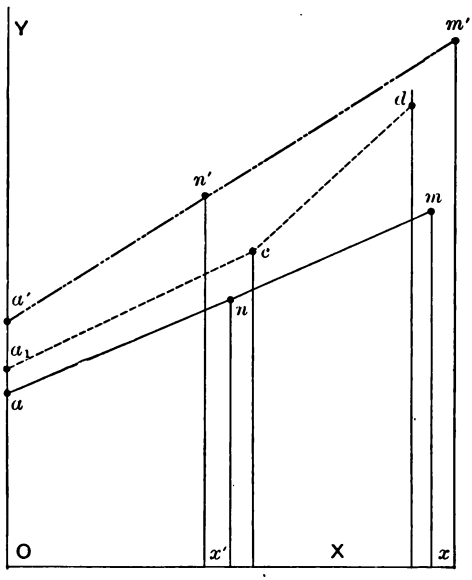


FIG. 6.

points with accents correspond to consumptions of denatured alcohol.

The records from the best engines show the curve slightly concave toward the axis of X; in good engines it practically coincides with a straight line; badly regulated engines are characterized by a curve with its convexity toward the axis of X (line, a_1cd).

Naturally the consumption, a, increases with the dimen-

sions of the engine, on account of the increase of frictional resistance.

As a first approximation, suppose that the curve of consumption per hour coincides with the straight line, $Y = a + bX$, a being the consumption at no load; b, a certain coefficient dependent upon the fuel, upon its satisfactory use in the engine, and on the good construction of the engine.

If the specific consumption, $\frac{Y}{X}$, is called y, then:

$$y = \frac{a}{X} + b.$$

Hence, y must ordinarily diminish as the power of the engine increases, for $\frac{a}{X}$ diminishes rapidly as the results of the experiments show.

On the other hand, for the same fuel, the more complete the utilization, the smaller b becomes. If b is assumed to be a constant, and if the values of X are taken for the abscissa, and the values of y as the ordinates, the preceding equation represents an equilateral hyperbola having for its asymptotes the axes of Y and the horizontal line, $y = b$.

A series of these asymptotes can be drawn: the smaller the value of b becomes for a given fuel, the more complete its utilization will be in the engine considered. From the results of the French competition tests, there may be calculated the fuel consumption per horsepower at half load and at full load at comparable speeds.

On the assumption that the frictional resistance does not vary, we may plot on a diagram the values of n for half load and m for full load, and have two points of a hyperbola. The smaller the value of b to which this hyperbola corresponds, the better the utilization of the fuel. All

engines yielding chords of the same hyperbola are on an equality as to utilization of the fuel, although having very different consumptions per horsepower per hour.

In other words a small engine, however perfect it may be, cannot be expected to have as small a relative consumption as a large engine.

The awards in the different groups of stationary engines at the Paris international competition of May, 1902, were distributed in accordance with the above described method of comparison, originated by Max Ringelmann, in connection with the competition of kerosene engines organized by the Agricultural Society of Meaux.

Comparison of alcohol with other fuels. — From what has been thus far indicated, it is evidently impossible to predict what efficiences may be attained in the near future with the various fuels when there has been more study of the preparation of the combustible mixture, and of the conditions of pressure, temperature, and speed.

Nevertheless we quote from Schöttler the following table to which are added the results obtained with the Brouhot engine, No. 25, in the Paris tests of May, 1902.

COMPARATIVE CONSUMPTION OF DIFFERENT FUELS.

	Date.	Metric Brake Horsepower.	Revolutions per Minute.	Fuel Consumption in Grams per Horsepower per Hour.	Calories Supplied per Horsepower per Hour.	Thermal Efficiency.
GASOLINE CALCULATED AT 10,000 CALORIES PER KILOGRAM.						
Güldner	1900	4.5	400	422	4,220	0.15
Deutz	1899	7.0	240	306	3,060	0.21
Banki	1900	25.0	210	221	2,250	0.28
KEROSENE CALCULATED AT 10,000 CALORIES PER KILOGRAM.						
Priestmann	1891	8.0	200	454	4,540	0.14
		12.0	200	323	3,230	0.20
Diesel	1900	30.0	180	204	2,040	0.30
ALCOHOL CALCULATED AT 6000 CALORIES PER KILOGRAM.						
Güldner	1900	3.5	380	766(?)		
Deutz	1900	14.0		450	2,700	0.24
ALCOHOL CALCULATED AT 5923 CALORIES PER KILOGRAM.						
Brouhot	1902	12.7	183	340	2,014	0.32
EQUAL VOLUMES OF ALCOHOL AND BENZENE CALCULATED AT 7880 CALORIES PER KILOGRAM.						
Brouhot	1902	16.3	199	233	1,835	0.34

These figures show that alcohol acts very satisfactorily in engines which run at relatively slow speed, better even than gasoline, and that the addition of benzene has little effect on the thermal efficiency. If it is considered that alcohol and gasoline are not sold by weight but by volume,

there is an advantage in favor of alcohol on account of its greater density. It may be hoped if the price of alcohol is not too high that alcohol engines will come into general use.

The good results with alcohol are due principally to the good carbureting, and to the fact that alcohol may be subjected to a high compression. The water contained in it diminishes the danger of pre-ignition. On this account in some alcohol engines the volume of the combustion chamber has been reduced to one seventh of the total volume of the cylinder.

CHAPTER VI.

CARBURETING.

Conditions to be fulfilled by carbureters. — The proportions of fuel and air should be quite exactly regulated to secure complete vaporization of the fuel and its uniform mixture with the air. The rate of feeding the fuel is generally regulated by trial by varying by hand the cross section through which the fuel flows under constant pressure. Vaporization of the fuel and heating of the air and mixture to a suitable temperature are usually accomplished by a more or less complete diversion of the exhaust gases, or by making use of the waste heat from the ignition burner.

Excess of air in the fuel mixture causes necessarily a loss of energy due to the increased amount of heat carried away in the exhaust gases; a sufficient excess of air would even produce incombustibility of the mixture. However, according to the tests at Paris in May, 1902, some excess of air is necessary, the amount varying from 0.3 to 0.7 of the quantity theoretically needed for combustion.

If C represents the per cent of carbon in the fuel, H the per cent of hydrogen, and O the per cent of oxygen, the additional amount of oxygen which it is necessary to introduce in order to secure complete combustion of the fuel will be represented by

$$\frac{32}{12}C + 8\left(H - \frac{O}{8}\right) = 8\left(\frac{C}{3} + H - \frac{O}{8}\right).$$

Since only about one fifth of the atmosphere is oxygen, the theoretical amount of air required will be, by weight,

$$40\left(\frac{C}{3} + H - \frac{O}{8}\right).$$

Usually the quantity of air is measured by the volume of the explosive mixture drawn into the cylinder by the piston during the suction stroke. This is too large a value for several reasons. First, the air contains water vapor, whose actual vapor pressure must be known. Second, the mixture is expanded by the heat obtained from the walls of the carbureter and of the cylinder. Third, at the end of the exhaust period, the burned gases from the preceding explosion remaining in the clearance space are generally under a pressure greater than the atmospheric pressure, and subsequently expand. If the admission valve is automatic, it does not open until the remaining burned gases have expanded enough to reduce their pressure to less than the atmospheric pressure by an amount sufficient to overcome the force of the valve spring. Hence, the incoming air enters during only a part of the suction stroke, and even then at reduced pressure. In some engines this disadvantage, which reduces the power of the engine in proportion to the reduction in volume of the entering air, is overcome by a mechanically operated admission valve or by a very large valve opening, and by reducing as low as possible the temperature of the burned gases as well as that of the explosive mixture, care being taken all the while to avoid condensation of any portion of the fuel mixture.

Since compression favors combustion, it is necessary to so arrange the compression and the amount of air as to avoid on the one hand an incombustible mixture, and on the other hand, pre-ignition.

But a lack of air is much more detrimental than an

excess of air, for there results incomplete combustion either of the carbon or of the hydrogen, or of both, and a corresponding loss of energy.

With alcohol, deficiency of air results in the formation of products which foul and corrode the cylinder walls and the valves, impeding and even preventing their action.

The adjustment of the carbureter is, then, the most difficult part of the operation of the engine; for the operator is guided only by the general running of the engine *when he is accustomed to it*, by the temperature of the admission pipe, by the temperature of the circulating water, and especially by the exhaust.

If combustion is complete the exhaust appears without color and almost odorless; but unfortunately the reverse is not always true, for even a scarcely perceptible smoke indicates bad combustion; however, in starting, a small amount of smoke may be ignored, it is only to be considered after the engine has become heated up. It is very seldom that during the first explosions of a well-regulated alcohol engine one may not see some smoke and perceive also the odor of formaldehyde; but these phenomena ought to be only temporary and ought not to occur again during operation.

In automobile engines, at least in those of high speed, perfection of carbureting may be partially sacrificed to secure greater simplicity of the mechanism. Moreover, the attention of the operator is constantly necessary while en route, on account of obstacles, changes of grade, of the wind, of the temperature, and of the condition of the road. According to conditions the chauffeur may vary the composition of the explosive mixture, although this generally can be done only at the sacrifice of economy. Besides, ordinarily the runs not being of great length and not following each other closely, there is time to examine and clean the parts of the

motor. But it is not so with stationary or portable engines.

It is certain that of all fuels used, coal is in most countries the cheapest. Thus it is necessary that the liquid fuels employed in explosion engines should offer some special advantages to compensate for their higher price.

For intermittent work, often an explosion engine is chosen, because a single turn of the fly wheel is sufficient to start it with full power, while a steam engine can only operate after the raising of steam pressure in the boiler, which in most economical boilers requires at least an hour. When the work is finished it is necessary to clean the grate of the boiler, a thing which requires further loss of time, and which increases, as does the starting, the general cost in proportion, which becomes larger as the length of operation is shorter.

Safety requires, moreover, the almost constant presence of an engineer to tend the fire, regulate the pressure, feed the boiler, and oil the machinery.

It is clear that if the almost constant attendance of an experienced operator should be necessary to regulate the carbureter with a stationary or portable explosion engine, the advantage of quick starting would become diminished if not entirely doubtful in comparison with the cost of the fuel.

It is necessary, then, that the carbureter when once regulated should stay practically so regulated that no irregular explosions resulting from bad combustion may occur, that no danger of change of the valves should be feared, and that the engine should require only the occasional inspection of some workman who needs only to see that the fuel tank and oil cups are kept filled and that the lubricators are working properly.

It is naturally also necessary that one should not be

obliged to take the engine to pieces for cleaning too frequently.

It is thus seen that conditions satisfactory for automobiles are far from being so for stationary or portable engines. Moreover, the latter are by their situations able to be supplied with accessories heavy and somewhat cumbersome, such as would not be permissible in a light vehicle.

Classification of carbureters. — The different forms of carbureters may be divided into five types, which will be briefly described and illustrated in succession, and a general criticism will be made of each type.

1. The substance to be vaporized contained in a vessel at constant level, is drawn at each double revolution through a mechanically operated valve and is converted into a spray in the current of air more or less warm. If a peep hole is put in the side of the passage way of the mixture there is seen very clearly a mist drawn along by the air. Such a mixture is evidently imperfect and on account of its lack of homogeneity it will present during combustion great irregularities; the combustion will generally be incomplete, there will be production of smoke, and in the case of alcohol there may possibly be attack upon the metal of the cylinder and of the exhaust valve. It may happen, however, that all the mixture enters the cylinder without leaving any deposit on the exterior of the admission valve; the latter will not be soiled, but the different particles of the mist will be forcibly separated in the cylinder. The heaviest will be thrown against the walls from which they will not vaporize easily, with the result that the final charge will be still less homogeneous than the initial mixture.

2. The fuel, raised by some sort of pump into a cup from which the excess returns by an overflow to the reser-

voir supplying the pump, is admitted at each suction stroke through an orifice more or less capillary, which coarsely sprays the fuel, into a chamber with a largely developed and often corrugated surface. In this chamber the fuel is supposed to be completely vaporized in contact with all or a part of the necessary air heated by the exhaust gases. The mixture is then drawn into the cylinder either directly or after mixing with the suitable addition of cold air.

The Niel carbureter (Fig. 8.) is of this type. If the constant level reservoir is sufficiently elevated and the orifice by which the fuel flows out is sufficiently small, the suction of the motor does not seem to cause appreciable variation in the rate of the flow; but it will appear later that for the liquids with which we are concerned, the variations of temperature of the capillary orifice influence to a marked degree the distribution.

Evidently this method may be modified by heating directly the surface onto which the liquid is projected, either by means of a diversion of a portion of the exhaust gases or by the waste heat of the lamp which heats the ignition tube.

3. Instead of an elevated constant level fuel reservoir the following arrangement may be used, which supplies the fuel only during the operation of suction of the engine. A reservoir, with constant level maintained by a float, is in communication with a tube, usually vertical, having its upper end at a level of a few millimeters above the surface of the liquid. The end of the tube is partially closed either by a needle valve or by the head of a conical screw, provided with fine grooves of a number and size dependent upon the capacity of the engine. At each suction stroke, as soon as the admission valve is open, there is produced in the suction tube a lowered pressure which draws in the

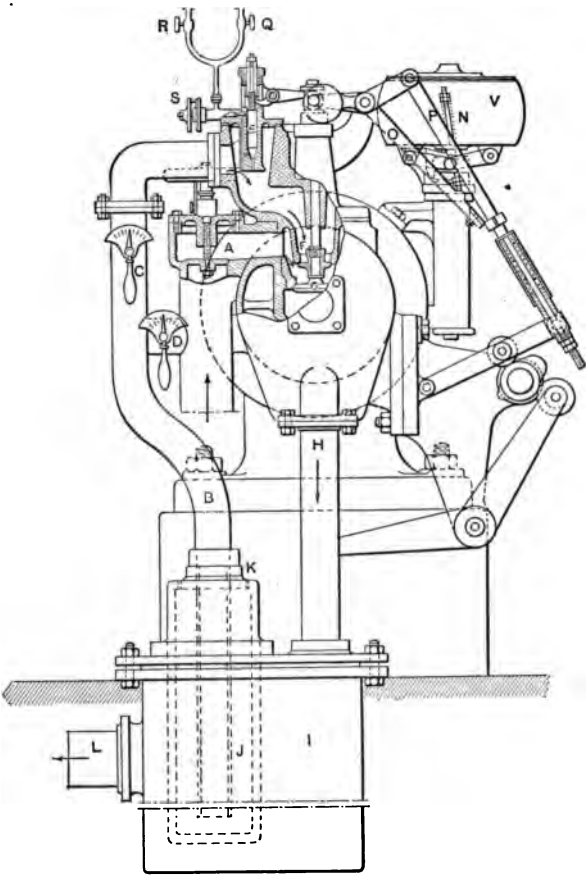


FIG. 8. SECTION OF THE NIEL ENGINE THROUGH THE CARBURETER.

A, cold air admission valve.— *B*, suction pipe for air warmed in the heater.— *C*, butterfly valve for regulating the warm air. — *D*, butterfly valve for regulating a diversion of the cold air.— *E*, needle valve for regulating and atomizing the fuel. — *F*, admission valve for the vaporized fuel. — *G*, admission valve for the mixture of cold air and the vaporized fuel. — *H*, exhaust pipe. — *I*, exhaust pot.— *J*, air heater. — *K*, holes for admitting cold air to the heater.— *L*, escape from the exhaust pot. — *V*, centrifugal governor. — *N*, rod moved by the governor and controlling the locking lever, O.— *O*, the locking lever.— *P*, spring operated bar, which controls the admission valve. — *Q*, connection for gasoline for use in starting. — *R*, connection for kerosene or alcohol. — *S*, hand lever for setting the needle valve.

exterior air and at the same time the fuel, which squirts out in very fine drops and is distributed through the current of air.

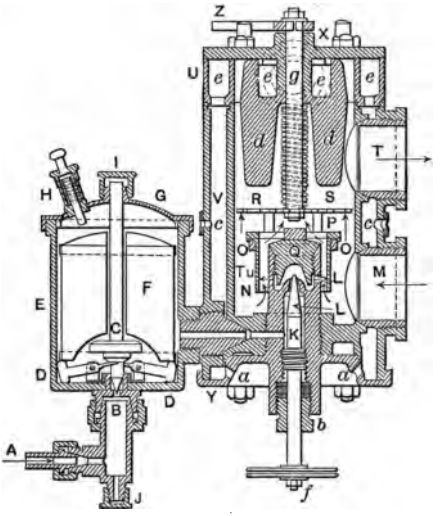


FIG. 9. LONGUEMARE CARBURETER.

A, supply pipe for alcohol. — *B*, a filtering conical union. — *C*, float chamber needle valve. — *DD*, pivoted levers.— *E*, constant level chamber.— *F*, float.— *G*, cover of constant level float chamber. — *H*, spring pin.— *I*, cleaning plug. — *K*, alcohol supply regulating needle valve.— *L*, *L'*, alcohol chamber. — *M*, entrance for air. — *Tu*, throttling tube. — *N*, air passageway. — *O*, serrations. — *P*, carbureting regulator. — *Q*, plug for closing the central chamber, *L'*.— *R*, perforated disk.— *S*, gas chamber.— *T*, outlet for explosive mixture. — *U*, heater with interior wings.— *V*, heating jacket. — *X*, carbureter cover. — *Y*, carbureter base. — *Z*, carbureter handle. — *a*, openings for heating the carbureter preliminary to starting. — *b*, packing gland. —*c*, *c*, holes for the escape of heating gases. — *d*, *d*, heating wings. — *e*, *e*, chambers in heater. —*f*, nut for setting the needle valve. — *g*, entrance tube for supplying hot gases to the heater.

Various arrangements are used to produce as intimate a mixture as possible between the air and the sprayed liquid. Some of these will be briefly described.

In the *Longuemare* carbureter (Fig. 9), the liquid is squirted around the needle valve, *K*, against the plug, *Q*, and is then deflected laterally through the small orifices, and meets a part of the current of air which has entered the lower part of the throttling tube, *Tu*. The quantity of air suitable for drawing in the fuel is regulated by the carbureter regulator, *P*. The remainder of the air mixes with the foggy mixture in passing through the perforated disk, *S*, and strikes upon the wings, *dd*, of the heater, as well as upon the lateral walls of the surrounding double walled jacket. For the use of denatured alcohol,

the jacket is first heated by burning a little alcohol under the carbureter. The hot gases from the burner enter at *a* and emerge at *c*.

In the *Martha* carbureter (Fig. 10), the nickel plated spray orifice, *A*, throws the fuel against the cap, *B*, which coarsely sprays it and deflects it against a stepped cone, *C*. The fresh air, filtered at *t*, the entrance to the passage *T*, draws along the liquid and its vapors through an Archi-

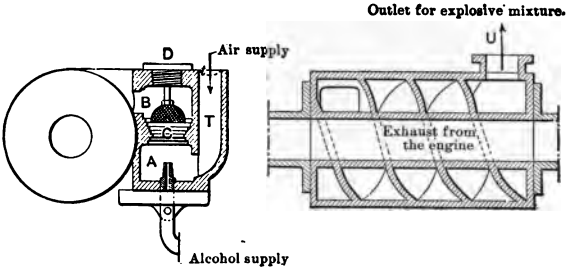


FIG. 10. MARTHA CARBURETER.

A, nickle-plated spray orifice. — *B*, metallic gauze basket. — *C*, steps. — *D*, plug for inspection. — *t*, metal gauze strainer. — *T*, air passage. — *U*, outlet tube for explosive mixture.

medean screw, usually perforated, within the axis of which is the exhaust pipe of the engine.

In the *Japy* carbureter (Fig. 11), the regulating float is concentric with the spray orifice. The liquid jet is drawn in by a current of fresh air controlled by the slide, *F*. The fuel is vaporized in the passage, *G*, which is connected to the admission valve and provided with exterior ridges heated by the surrounding case, *H*, in which circulates either part of the exhaust gases, or water supplied from the cylinder jacket. When the engine is to be run on alcohol, it is started by putting a few drops of gasoline into the orifice, *D*, which is then covered with a ring.

In the *Charron* carbureter (Fig. 12), we find again a pressure reservoir. A valve, *I*, controlled by the governor, allows the fuel to pass into the current of heated air controlled by the cock, *C*. The fresh air enters by the tube, *D*, is heated in the vessel, *G*, placed in the exhaust chamber, *H*; a diverting tube, *E*, supplied with a butterfly valve, permits the temperature to be regulated by taking in a suitable proportion of cold air. The valve, *J*, when operated serves for admission and vaporization.

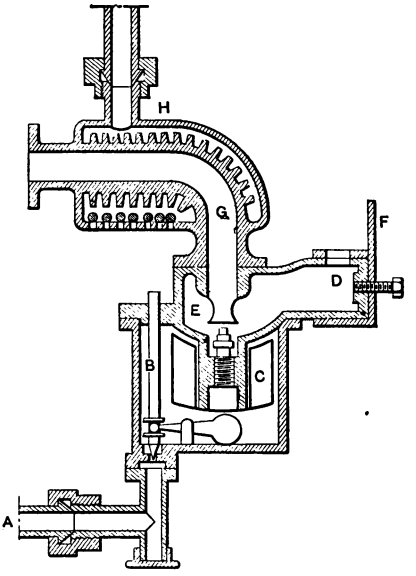


FIG. 11. JAPY CARBURETER.

A, liquid fuel supply pipe. — *B*, needle valve regulating fuel supply. — *C*, float which maintains constant level. — *D*, air entrance. — *E*, mixing chamber for air and liquid. — *F*, valve which regulates supply of air. — *G*, passage leading to admission valve. — *H*, surrounding jacket in which a part of the exhaust gases or of the cylinder cooling water passes.

It is apparent that in most of the apparatus of this class the attempt is made to spread out the liquid with a large surface exposed to the air. We shall see later that this arrangement permits a selection among the different constituents of the fuel, when it is a mixture of different substances, and if the temperature of the air is insufficient to cause a complete and instantaneous vaporization of the fuel. Since at each stroke the lowered pressure varies between two minima, there are very rapid differences in the flow through the spraying orifice. This flow, according

to Poiseuille, is proportional to the decrease in pressure, or perhaps varies more rapidly than the fall of pressure, since the ratio of the length to the diameter of the capillary

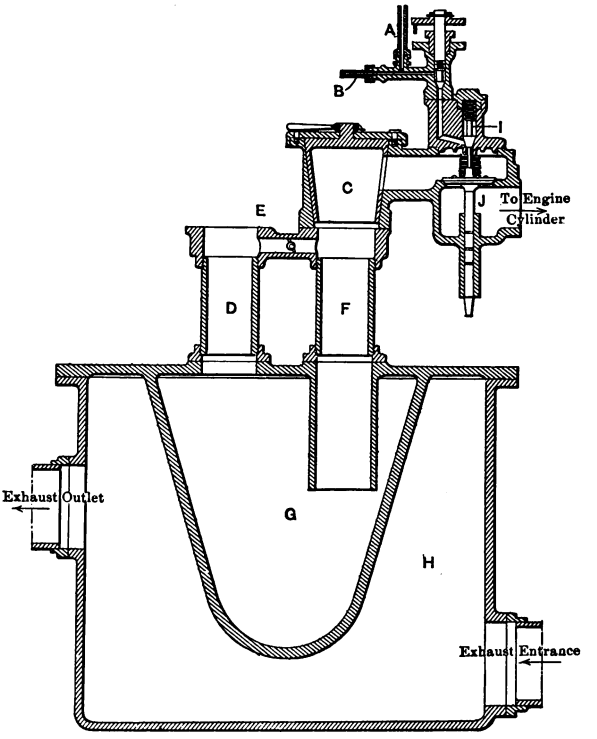


FIG. 12. CHARRON CARBURETER.

A, gasoline supply pipe. — *B*, alcohol supply pipe. — *C*, stop-cock for warm air. — *D*, entrance for cold air. — *E*, butterfly valve for regulating the temperature. — *F*, warm air pipe. — *G*, air heating chamber. — *H*, exhaust chamber. — *I*, valve controlled by the governor and serving to introduce the liquid fuel. — *J*, valve for admission and atomizing.

orifice is small. On the contrary, the inflow of air varies as the square root of the fall of pressure. When at the existing temperature the liquid is in excess of the amount

which can be totally and instantaneously vaporized by the amount of air present, there will be fractional distillation of the most volatile portions of the liquid, and the less volatile portions will be carried along in the form of small drops. If an attempt is made to obtain contact by the use of metallic gauze, the small drops will be retained when the suction is reduced and will be drawn along in the

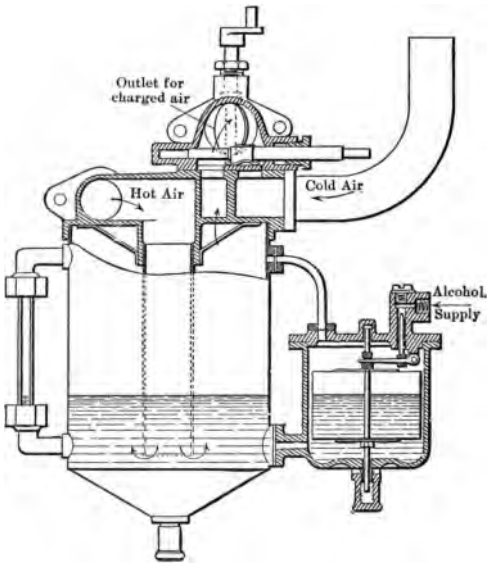


FIG. 13. CARBURETER OF BUBBLING TYPE.

liquid state during the next suction stroke. It will be useless to present afterwards hot surfaces to the gaseous current, which will remain supersaturated with the less volatile parts whose liquid particles will be deposited and decomposed on the exterior surface of the admission valve and on the walls of the cylinder and piston. In any case there will be stratification of the gaseous mixture and poor

combustion. This is what the author has found in the greater number of the motors furnished with spray carbureters, especially in engines of very high speed.

Moreover, we shall see that for many liquids and especially for alcohol mixtures, the rate of flow through a capillary orifice varies rapidly with the temperature.

4. Next come the type of apparatus in which carbureting is secured either by drawing the air over the surface of the liquid, or by bubbling the warm air through a small volume of the liquid supplied by a constant level chamber. The charged air is then mixed with a suitable quantity of cold air. If the liquid is not homogeneous it is evident that the less volatile portions will be rapidly concentrated in the liquid which will become, therefore, less and less suited to the process of carbureting. Fig. 13 shows an apparatus of this type.

5. The last type of carbureters is one in which, at each useful suction, there is supplied a definitely measured charge of the fuel.

In the Gobron-Brillié carbureter (Fig. 14), the supply of fuel is furnished by means of a wheel, *C*, containing small cells, *e*, and operated by a ratchet wheel, *G*, of which the number of teeth equals the number of cells. Each cell, in passing before a little semi-circular canal, is exactly filled with the liquid, and later arrives at the point of convergence of two pipes, one of which, *L*, brings the air heated by contact with the exhaust pipe, and the other, *P*, leads to the gauze, *T*, for spraying the liquid. The air draws along the liquid fuel into the chamber of the admission valve, *E*. An eccentric operates the ratchet of the distributer and the governor acts by stopping the action of the ratchet when the speed becomes too great.

It is evident that to make the best use of the engine it

is necessary to vary the capacity of the cells, according to the nature of the fuel.

With some liquids complete vaporization does not take

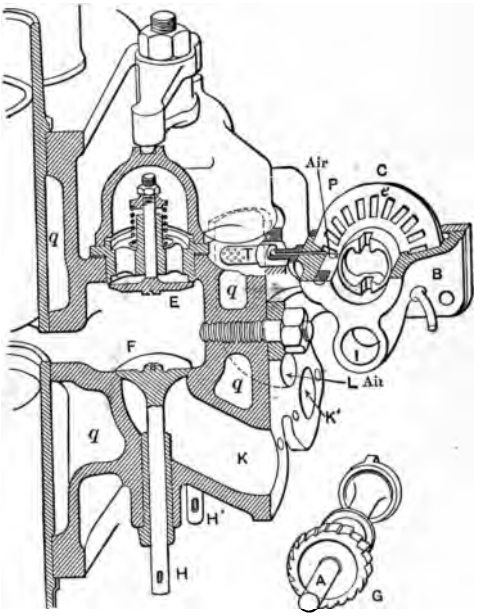


FIG. 14. GOBRON-BRILLIÉ CARBURETER.

A, shaft of the wheel, *C*. — *B*, box for the wheel, *C*. — *C*, conical distributer wheel with ring of small cellular recesses. — *G*, ratchet wheel which operates the distributer. — *E*, automatic admission-valve. — *F*, exhaust valve. — *H*, *H'*, exhaust valve rods. — *K*, *K'*, exhaust pipes. — *L*, *P*, entrance pipes for the air (the pipe, *L*, contains a valve for regulating the suction). — *T*, gauze for atomizing the liquid. — *q*, *q*, waterjacket.

place, the engine smokes, and the surfaces are encrusted.

The Brouhot carbureter avoids this criticism. It has two parts, a distributer with capacity variable according to the fuel used (Fig. 15), and a vaporizer (Fig. 16).

In the distributer, a constant level float, *D*, operates a

needle valve, *B*, which controls the supply of fuel through the small tube, *A*. The liquid rises to a constant level in the distributing chamber, *F*, through the orifice, *E*. The valve, *H*, mechanically lifted, when a charge of fuel is needed by the engine, permits the liquid to fill the cavity between the lower valve, *I*, and the piston, *K*. The position of the piston, *K*, is set by the nut, *L*, moving on the rod, *J*, which is graduated so that the position, corresponding to each fuel used, may easily be returned to. Thus, the carbureting may be varied even while the engine is running. The valve, *H*, closes, thus including a known volume of fuel. Then under the control of the governor, the valve, *I*, is opened, permitting the measured liquid to flow out and meet the air sucked in through the tube, *M*, in the proper quantity. The mixture then flows through *N* toward the vaporizer.

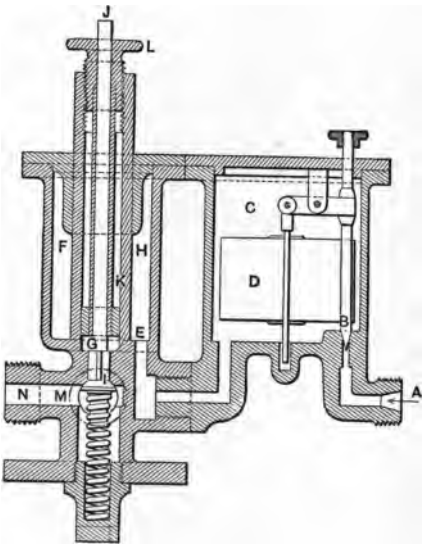


FIG. 15. BROUHOT DISTRIBUTER.

A, fuel supply pipe. — *B*, float chamber needle valve. — *C*, constant level float chamber. — *D*, float. — *E*, passage to distributing chamber. — *F*, distributing chamber. — *G*, fuel measuring chamber. — *H*, fuel measuring valve. — *I*, fuel outlet valve — *J*, rod operating outlet valve, *I*. — *K*, piston which determines size of fuel measuring chamber. — *L*, nut for setting piston, *K*. — *M*, air supply pipe. — *N*, fuel and air mixture outlet pipe.

The mixture enters the vaporizer at *G* (Fig. 16), and rises from top to bottom through the turns of a hollow helix and emerges through *L* to pass to the automatic

admission valve, *M*. It passes on the way an additional opening for pure air regulated by the valve, *J*. *O* is the

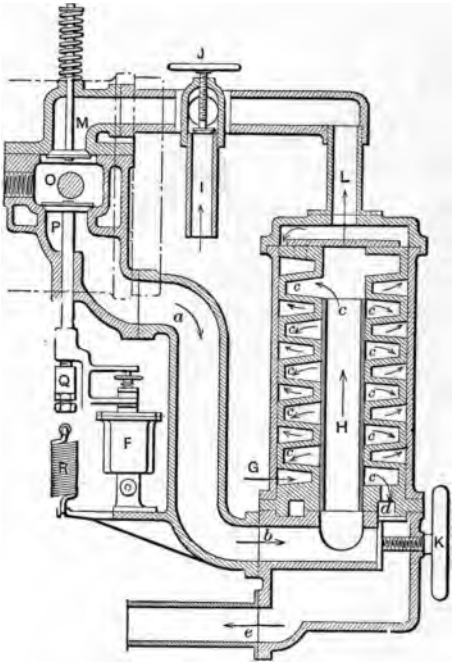


FIG. 16. BROUHOT VAPORIZER.

F, fuel distributer shown in Fig. 15. — *G*, entrance of fuel and air mixture to vaporizer. — *L*, outlet from vaporizer for heated fuel mixture.— *I*, pipe for supplying additional air. — *J*, valve controlling additional air supply. — *M*, automatic admission valve. — *O*, spark plug opening. — *P*, exhaust valve.— *Q*, lever operating exhaust valve and fuel distributer, *F*.— *R*, exhaust valve closing spring. — *a*, *b*, exhaust passage to vaporizer. — *K*, valve wheel controlling proportion of exhaust to pass through vaporizer by means of passage, *H*, *c*, *e*, *d*.

orifice in the valve chamber through which the spark plug is inserted.

A lever, *Q*, opposed by the spring, *R*, acts simultaneously

on the exhaust valve and on the valve, *H*, of the distributer in such a way as to make them move completely or not at all.

The exhaust passes through a pipe, *ab*, but a valve controlled by the wheel, *K*, forces part of the burned gases to rise through *H*, then to follow the path, *cc-d*, between the hollow turns of the helix so as to provide the temperature necessary for the complete vaporization of the fuel. The gases pass out through *d*, rejoining the general exhaust, *e*.

The same apparatus after suitable regulation may be used for gasoline, pure or carburated alcohol, kerosene, etc. The change may be made while the engine is running.

There exist numerous other distributers and carbureters, but they may be classified under one of the types of which characteristic examples have been given.

CHAPTER VII.

TEMPERATURE OF VAPORIZATION.

The various fuels to be studied. — As heretofore, it appears useful to compare with alcohol the various liquid fuels used in explosion engines.

The alcohol used for denaturing need not be chemically pure. It is sufficient if it is 90 to 95 per cent in strength, and contains no more than 1 per cent of the higher homologs of ethyl alcohol.

In France the usual process of denaturing alcohol intended for engines and for lighting and heating is to add to 100 volumes of 90 or 95 per cent alcohol 10 volumes of methyl alcohol, indicating 90 per cent at 15° C., and 0.5 volume of benzene.

The methyl alcohol is not pure methyl alcohol, it is a crude mixture, as said, indicating 90 per cent at exactly 15° C., and contains various pyrogenic bases, which give it a penetrating odor, and also contains at least 25 per cent of acetone.

The benzene is not pure benzene, but is a mixture of residues from the distillation of benzol (toluene, xylene, cymene, etc.) boiling at 180° to 220° C.

The benzene with which the alcohol is carburated is, on the contrary, the true coal benzene; in the experiments of November, 1901, 90 per cent benzene was used; in those of May, 1902, pure benzene was used for the stationary engines.

The author has not experimented with other carburated alcohols, but it should be noted that some engineers add to the mixture 5 to 6 per cent of kerosene in order to give

to the mixture some lubricating property. Others try to substitute gasoline for coal benzene. When the proportion of the oil is large, the mixture is stable only if but a small proportion of water is present, and if 8 to 12 per cent of concentrated amyl alcohol is used as a solvent. It is necessary to be confined to 95 per cent alcohol and to amyl alcohol boiling at 132° C and dehydrated with lime, in order to obtain mixtures which do not separate into two parts at — 17° C, a temperature which may be met in winter.

In order to obtain consistent results there were employed for the alcohol mixtures used in the author's experiments only substances as pure as possible.

In the case of the hydrocarbons of the petroleum series

PHYSICAL PROPERTIES OF THE C_nH_{2n+2} SERIES.

Formula.			Boiling Point, Degrees C.	Specific Gravity at Temperature Indicated.	
Pentane	Normal	C_5H_{12}	37–39	0.626	(17°)
	Iso	C_5H_{12}	30.5–31.5	0.628	(18°)
Hexane, normal*		C_6H_{14}	69–71	0.663	(17°)
Heptane, normal†		C_7H_{16}	98	0.688	(15°)
Octane	Normal†	C_8H_{18}	124	0.719	(0°)
	Isomere		119–120	0.719	(17°)
Nonane	Normal	C_9H_{20}	149.5	0.723	(13.5°)
	a N‡	C_9H_{20}	135–137	0.742	(12°)
	b N‡		129.5–131.5	0.734	(12.7°)
Decane		$C_{10}H_{22}$	158–159	0.736	(18°)
			161	0.757	(16°)
Undecane		$C_{11}H_{24}$	180–182	0.756	(16°)
Dodecane		$C_{12}H_{26}$	214.5	0.755	(15°)
Tredecane		$C_{13}H_{28}$	218–220	0.778	(15°)
Tetradecane		$C_{14}H_{30}$	236–240	0.796	....
Pentadecane		$C_{15}H_{32}$	258–262	0.809	....
Hexadecane		$C_{16}H_{34}$	towards 280	0.771	....

* Chief constituent of gasoline.

† Chief constituent of ligroin.

‡ These two nonanes are the first constituents of kerosene which continue up to $C_{16}H_{34}$ with some substances of the formula C_nH_{2n}.

this was not true on account of the enormous loss of time and the expense which such a purification would have entailed. Since these mixtures were studied only for comparison, simple fractional distillation was resorted to in order to separate the lighter portions from the heavier parts. In the first experiments, simple distillation as employed in commercial tests was used. Later rectification was employed in order to recover more accurately the more volatile products boiling up to 72° C. Above that, the apparatus clogged up. It is well known that the results of distillation or rectification vary with the speed of the operation; the heat was so regulated as not to recover more than two drops per second.

In order to understand the results which follow, there are given on page 129 the physical properties of the different hydrocarbons of the saturated series that occur in the

HYDROCARBON ENGINE FUELS TESTED DURING THE SUMMER OF 1902.

Tenths.	Temperature in Degrees Centigrade.	Specific Gravity.	Substances Collected.
AUTOMOBILINE (SPECIFIC GRAVITY = 0.699).			
1	58–64–68	0.664	Traces of isopentane, mixture of hexane and heptane.
2	68–72	0.669	
3	72–76	0.678	
4	76–81	0.687	Chiefly heptane.
5	81–87	0.694	
6	87–95	0.704	
7	95–101	0.725	Heptane to normal nonane.
8	101–109	0.714	Nonanes.
9	109–127	0.733	
STELLINE (SPECIFIC GRAVITY = 0.669).			
1	45–50–52	0.649	Mixture of pentane and hexane.
2	52–53	0.647	
3	53–58	0.653	
4	58–63	0.678	
5	63–67	0.666	
6	67–71	0.673	Hexane and heptane.
7	71–79	0.686	
8	79–89	0.698	Heptane and octane.
9	89–120	0.715	Octane.

gasoline and kerosene oils, which have not been submitted to the heat decomposition known as *cracking*.

Besides this saturated series there are found some of the ethylene series and some benzene derivative sometimes called naphthene, having the same formula as the ethylenes, $C_n H_{2n}$, but distinguished from them by indifference toward concentrated sulphuric acid.

It appears that the lighter oils at the disposal of owners of explosion engines are not selected according to a very definite principle. It is sought simply to have a mixture

HYDROCARBON ENGINE FUELS TESTED DURING THE SUMMER OF 1902. *Continued.*

Tenths.	Temperature in Degrees Centigrade	Specific Gravity.	Substances Collected
BENZOMOTEUR (SPECIFIC GRAVITY = 0.684).			
1	42–60	0.648	Mixture of pentane and hexane.
2	60–63	0.655	
3	63–68	0.665	Hexane.
4	68–71	0.670	
5	71–75	0.675	
6	75–83	0.686	Hexane and heptane.
7	83–88	0.693	
8	88–96	0.704	
9	96–106	0.718	Heptane.
MOTONAPHTA (SPECIFIC GRAVITY = 0.705).			
1	45–66	0.655	Traces of pentane.
2	66–70	0.664	Hexane.
3	70–77	0.676	Hexane and heptane.
4	77–84	0.688	
5	84–90	0.701	
6	90–101	0.713	
7	101–112	0.726	
8	112–123	0.814	Nonane and decane.
9	123–160	0.749	
KEROSENE (SPECIFIC GRAVITY = 0.801).			
1	138–177	0.755	Nonane to undecane.
2	177–197	0.765	Undecane and dodecane.
3	197–212	0.776	Dodecane and tredecane.
4	212–236	0.783	Tredecane and tetradecane.
5	236–253	0.796	Tetradecane.
6	253–274	0.795	Pentadecane and hexadecane.

sufficiently rich in very volatile ingredients to facilitate the carbureting and the explosion of the remaining portion and to keep approximately within a limiting density fixed to 134 by custom. But this density is not a safe guide, for it may correspond to a single very volatile body like hexane, or to an indefinite mixture of lighter and heavier bodies.

This is shown by the tables on pages 130 to 134. The first set gives the results of simple distillation of engine fuels purchased in the market during the summer of 1902; the second, the results of fractional distillation of the same fuels, purchased in the autumn of the same year.

Only the first were used in the experiments of which the results are given later.

It is apparent that the fuels sold for engines may contain some butane but that hexane and heptane predominate, while many contain some of the still heavier compounds.

BENZOMOTEUR (SPECIFIC GRAVITY = 0.7125 at 15° C).

	Temperature in Degrees Centigrade.	Volume Collected in Per Cent.	Specific Gravity of the Distillate at 15° C.	Substances Collected.
Rectification.	25 - 35	6.30	0.625	Isopentane.
	36 - 64.5	8.5	0.658	Hexane and heptane.
	64.5- 69	9.0	0.681	
	69 - 72	6.3	0.694	
		30.1		
Direct Distillation.	90 -91	6.0	0.717	Heptane, octane and α nonane.
	91 - 94	6.1	0.718	
	94 - 98	6.1	0.722	
	98 - 99	6.0	0.724	
	99 -102.5	7.5	0.727	
	102.5-105	6.0	0.729	
	105 -108	6.1	0.730	
	108 -112	6.0	0.733	
	112 -119	6.0	0.737	
	119 -128	6.0	0.742	
	Residue	7.5	0.752	
	Loss	1.5		
		100		

The observations contained in the tables on pages 130 and 131 relate simply to the predominant ingredients, assuming that they are not accompanied by naphthenes.

STELLINE (SPECIFIC GRAVITY = 0.700 AT 15° C).

	Temperature in Degrees Centigrade.	Volume Collected in Per Cent.	Specific Gravity of the Distillate at 15°C.	Substances Collected.
Rectification.	12 – 29	3.1	0.623	Butane and isopentane.
	29 – 32	2.0	0.625	"
	32 – 33.5	1.1		
	33.5– 37	3.1	0.631	Isopentane and normal pentane.
	37 – 40	1.0		
	40 – 41.5	0.4		
	41.5– 51	0.4	0.663	Pentane and hexane.
	51 – 63	1.9		
	63 – 66	3.5		
	66 – 67.5	6.0	0.675	
	67.6– 69	6.8	0.678	Hexane and heptane.
	69 – 71.5	5.8	0.684	
		35.1		
Direct Distillation.	85 – 88.5	5.8	0.705	
	88.5– 91	5.8	0.706	
	91 – 94	6.2	0.709	
	94 – 97	6.0	0.714	
	97 – 99	7.0	0.718	
	99 –103	7.0	0.720	
	103 –105	7.0	0.720	
	105 –108	3.5	0.727	Heptane, octane and α nonane.
	108 –112	3.5		
	112 –115	1.7		
	115 –119	2.0	0.733	
	119 –123	1.6		
	123 –127	1.8		
	Residue	4.0	0.745	α Nonane.
	Loss	2.0		
		100		

The table on pages 132 to 134 gives the results obtained by distillation and rectification in October, 1902. The specific gravities of the initial mixtures differ materially from the specific gravities shown in the preceding table.

Investigation of vapor pressures. — In order to understand how to secure complete vaporization of the liquid

AUTOMOBILINE (SPECIFIC GRAVITY = 0.703 AT 15° C).

	Temperature in Degrees Centigrade.	Volume Collected in Per Cent.	Specific Gravity of the Distillate at 15°C.	Substances Collected.
Rectification.	12 – 26	0.5	0.622	Butane.
	26 – 30	0.8		
	30 – 32	2.0	0.628	Butane and isopentane.
	32 – 33	8.7		
	33 – 34	1.7	0.630	Isopentane and pentane.
	34 – 36	1.5		
	36 – 42	1.6		
	42 – 60	3.0	0.671	Hexane and heptane.
	60 – 63	3.5		
	63 – 64	2.0		
	64 – 66	6.2	0.677	
	66 – 67.5	6.4		
	67.5– 71.5	6.4	0.690	
	71.5– 77	3.4	0.708	
		47.7		
Direct Distillation.	90 – 98	6.0	0.723	Octane and various hydrocarbons.
	98 – 99	6.0	0.725	
	99 –102	6.2	0.726	
	102 –105	6.2	0.728	
	105 –108	6.0	0.728	
	108 –122	6.5	0.737	Nonanes.
	122 –139	6.1	0.746	
	Residue	6.8	0.773	Pentadecane.
	Loss	4.5		
		100		

fuels in the quantity of air necessary for complete combustion, it is essential to know the relation that exists between the temperature and the vapor pressure of the fuels. Numerous works deal with this subject, but they usually relate only to pure substances, while all liquid fuels are mixtures. Hence, it was necessary to employ special methods. When a pure substance is used, all traces of dissolved gas can be removed by prolonged boiling, and vapor can be produced without changing the original substance. Hence a reduced sample can be used

for study. It is very different in the case of mixtures which are modified through distillation if they are boiled, or if a very small weight is exposed to a large amont of air.

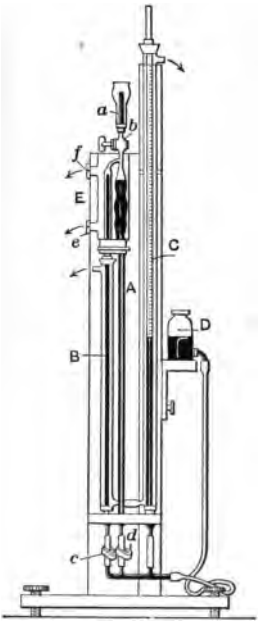


FIG. 17. APPARATUS FOR MEASURING THE VAPOR PRESSURE OF LIQUID MIXTURES.

Hence the new apparatus shown in Fig. 17 was devised. A barometer tube, *A*, whose upper end has been enlarged into a bulb having a capacity of 75 or 80 cubic centimeters, is terminated at its upper end by a capillary tube to which a well ground stopcock, *b*, is sealed, for supplying the mercury. The capillary tube extends 20 centimeters above the stopcock. Along this prolongation there slides a cork holding a funnel shaped tube containing some mercury in its lower part. When this funnel is pushed down, the end of the capillary tube is uncovered, and the liquid to be studied may be introduced into the tube, *A*. Next the funnel is raised so that the capillary tube may be immersed and filled with mercury by suction. Then the sealing up is perfect and a vacuum can be made in the barometer tube without any air being able to get in. If liquids capable of dissolving fats are experimented on, pressure must not be used in manipulating this apparatus, for gases or vapors would escape between the stopcock key and its enclosure.

The enlarged part of the tube, *A*, is plunged into a bath, *E*, having two lateral tubes, *e* and *f*. This bath is kept at

a constant temperature by means of a thermo-syphon, regulated by a delicate thermo-regulator.

The lower end of the capillary tube is connected to another capillary tube doubly curved, to render it elastic. This second capillary tube bends downwards and joins the tube, *A*, to a second tube, *B*. The tubes, *A* and *B*, form with another tube, *C*, an open manometer. The tube, *B*, has on its upper part a circular mark corresponding to the zero mark on the tube, *C*. A small-sized flask, *D*, supported, as in Schloesing's eudiometer, on a movable shelf, is connected by a long, thick, desulphurized rubber tube with the three tubes, *A*, *B*, and *C*, and regulates the level of the mercury in these tubes. Pinchcocks, *c* and *d*, serve to shut off communication with the tubes, *A* and B.

The tubes, *B* and *C*, are surrounded by larger tubes in which circulates a liquid (water containing 10 per cent of formalin to procure sterilization).

The whole mechanism is mounted on a solid base provided with leveling screws to make the tubes perfectly vertical.

To use the apparatus, it is first filled completely with mercury; the air is driven out through the stopcock, *b*, by raising the flask, *D*, to a suitable height. The liquid in the jacket, *E*, is raised to a temperature slightly less than the boiling point of the liquid to be tested. The pinchcock, *c*, is closed, and the liquid to be tested is poured into the funnel. The jar, *D*, is lowered a suitable amount. The stopcock, *b*, is slightly opened to admit the liquid little by little, until the enlarged part of tube, *A*, is filled. Then the funnel tube, *a*, is raised to fill the capillary tube with mercury, and stopcock, *b*, is closed. The jar, *D*, is lowered as far as it will go, by which a partial vacuum is produced and boiling sets free the dissolved air. Then the

pinchcock, *d*, being closed, the pinchcock, *c*, is opened to increase the size of the vapor chamber and to cause a new active boiling. When this is finished the jar, *D*, is raised so that the mercury flows from *B* into *A* stirring up the liquid and aiding the expulsion of the air until the apparatus is almost completely filled, except for one or two cubic centimeters that are occupied by the extracted gases. These are quickly let out through the stopcock, *b*. This operation is repeated until it is evident that there are no longer any residue dissolved gases. In this way all the dissolved gases are driven off; and only a negligible amount of the most volatile components of the liquid under investigation is carried away.

The best way is to start the operation in the evening in order that by the next morning the temperature of the bath may be that of the surrounding air.

Before commencing operations the jar, *D*, is lowered and the pinchcock, *d*, slowly opened, so as to form in the tube, *A*, a vapor chamber only a few centimeters in volume, then the pinchcock is closed. The bath, *E*, is brought to the desired temperature, and the level of the mercury in *B* is brought to the zero mark. The temperatures of the bath, of the jacket of cold water after renewal, are read, as well as the difference of level in the two branches of the manometer and the corrected barometric height. The necessary corrections are made to bring to 0° the differences of level found between the two columns of mercury.

The author's experiments give figures that coincide almost exactly with those of Ramsay and Young for two pure hydrocarbons, isopentane and hexane.

The following table shows the manner in which the pressures of the vapors of hydrocarbon compounds vary whether the vapors are pure or are the mixtures tested by the author in the summer of 1902.

VAPOR PRESSURE OF VARIOUS HYDROCARBON FUELS AT DIFFERENT TEMPERATURES.

Temperature in Degrees Centigrade.	Vapor Pressure in Millimeters of Mercury.									
	Iso-pentane.	Hexane.	Auto-mobiline.	Automo-biline, First Tenth.	Stelline.	Stelline, Ninth Tenth.	Moto-naphta.	Benzo-moteur.	Kero-sene.	Benzene.
−30	58	7	...	...	...	...	...	...	...	...
−20	100	14	...	...	...	...	...	...	...	...
−10	164	26	...	...	...	...	...	...	...	14.8
0	258	45	99	227	164	42	152	162	16	27
5	319	58	115	259	190	48	170	181	17	36
10	390	74	133	296	220	55	191	203	19	45
15	475	95	154	336	255	63	214	228	22	61
20	572	119	179	384	296	72	240	255	24	77
25	690	154	210	447	358	83	260	286	28	96
30	815	184	251	522	433	99	292	320	30	120
35	...	228	301	607	512	119	345	364	34	156
40	...	276	360	715	596	139	413	416	39	188
45	...	335	422	839	685	166	496	475	43	224
50	...	401	493	...	792	198	575	536	48	271
55	...	482	561	...	..	233	660	617	53	326
60	...	567	648	...	...	278	768	725	59	390
65	...	674	739	...	...	330	...	812	67	468
70	...	785	846	...	...	383	...	...	76	557
75	...	...	...	...	...	438	...	...	87	656
80	...	...	...	...	...	498	...	...	100	758

VAPOR PRESSURE OF ETHYL ALCOHOL OF DIFFERENT STRENGTHS AND AT VARIOUS TEMPERATURES MEASURED IN MILLIMETERS OF MERCURY.

Temperature in Degrees Centigrade.	Strength of Alcohol in Per Cent by Volume.										
	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
0	4.5	...	...	...	...	...	..	..	..	12.7	12.2
5	6.5	...	...	...	...	...	..	...	..	18	17.5
10	9.1	...	...	...	...	...	..	...	..	24	23.7
15	12.7	...	...	...	...	...	..	...	..	31	33.6
20	17.4	...	...	...	...	...	..	...	..	39	43.8
25	23.5	...	...	...	...	...	..	...	..	57	60
30	31.5	42	50.6	58.5	63.5	67.5	71	72	73	75.5	78.1
35	41.8	55	66.5	76	148	89	96	99	101	101.6	105
40	54.9	73.5	89	100	109.5	114.5	124	132	133	134.6	140
45	71.4	98	116.5	129	142	148	162	174	177	178	179
50	92.0	127	152	168	182.5	190	218	220	221	221	221.5
55	117.5	167	197	215	236	257	277	280	281	281.5	282.5
60	148.9	210	247	270	295	323	343	346	348	349	350.2
65	187.1	269	306	333	363	393	412	424.5	433	438.5	441
70	233	325	377	411	449	479	497	514	529	539	544.9
75	289	397	461	506	553	589	604	617	635	641	655
80	354	490	564	615	665	700	717	735	760	783	811.8

It is seen that the various hydrocarbon fuels examined during the summer of 1902, lie from a point of view of vapor pressure between isopentane and hexane, that is, their pressure depends mainly on that of the most volatile parts, although these represent only a small fraction of the total mass. A selective vaporization must be expected at a low temperature when air comes into the presence of an excess of these mixtures.

Since ethyl alcohol is very widely used, it seemed worth while to include the vapor pressure of its mixtures with water even below the limits possible for use as fuel.

The increase of vapor pressure for mixtures of alcohol and water is far from following a regular law. In the neighborhood of the point where the mixture has the maximum concentration of volume, the vapor pressure varies slowly as the quantity of water varies, the temperature being constant.

When the vapor pressure of a given mixture of water and alcohol is represented on a diagram, the curve is usually continuous. But near mixtures corresponding to maximum contraction, the curve abruptly stops and is replaced by a straight line, making a greater angle with the axis of temperature than the tangent at the limiting point of the curve.

The lines are straight between the following limits:

Per Cent of Alcohol by Volume.	Between the Temperatures in Degrees, C.	Extreme Vapor Pressures in mm.
43.8	49.8 to 67.7	184–438
54.6	47.5 to 67.5	168.5–439
59.2	43.2 to 64.	138–400

The same condition is found with mixtures of denatured alcohol and pure benzene. This phenomenon may be more interesting theoretically than practically.

The vapor pressure of these mixtures is not intermediate between the pressures of the component constituents at the same temperature, but is always appreciably superior to that constituent having the greater pressure, and the variations in the vapor pressure of the mixture due to a change in the relative proportions of the ingredients are very slight.

This is shown in the following table:

VAPOR PRESSURE OF VARIOUS ALCOHOL MIXTURES IN MILLIMETERS OF MERCURY.

Temperature in Degrees Centigrade.	Acetone.	Methyl Alcohol.		Methyl Alcohol and Acetone.		Alcohol Denatured by A.	Carburated Alcohol Containing Denatured Alcohol by Volume.		
		99 Per Cent.	90 Per Cent.	Alcohol, 75, Acetone 25, Per Cent. (A)	Alcohol, 50 Per Cent. Acetone, 50 Per Cent.		75 Per Cent.	50 Per Cent	28.6 Per Cent.
0	63	29.6	29	52	61	15	41	43	62
5	81	43	42	67	77	20	52	55	73
10	110	55.2	54	85	97	27	66	69	86
15	154	83	80	108	122	37	84	87	101
20	182	109.5	104	131	147	51	102	106	121
25	227	141	129	161	182	68	130	138	148
30	280	182	162	204	227	92	163	177	180
35	337	232	209	262	286	117	205	218	219
40	403	293	266	327	352	151	255	262	263
							(44)298	(43.5)296	(41.3)274
45	487	361	330	401	424	192	310	319	337
50	582	435	399	478	503	238	390	403	415
									(54.5)490
55	690	539	481	576	600	293	453	488	496
							(57.7)524	(57.7)534	
60	814	627	583	691	711	363	564	590	605
65	939	762	716	809	838	445	674	704	740
70	...	...	884	...	...	538	795	820	884
75	...	...	...	...	...	645	...	...	...
80	...	...	...	...	...	810	...	...	...

NOTE. — The figures in parentheses in the last three columns show the temperatures between which the vapor pressure curves of denatured and carburated alcohol are replaced by straight lines.

It is evident that the addition of an impure methyl alcohol increases slightly the vapor pressure of 90 per cent ethyl alcohol, and its carburation with pure benzene makes the vapor pressure curve almost coincide with the curve of hexane. Hence, it is useful to carburate the alcohol to assist in volatilization of the fuel as well as to increase the available energy.

The diagram (Fig. 18) shows better than the numerical tables the way in which the vapor pressures vary as functions of the temperature.

For each substance when no permanent gas is present, the vapor pressure curve divides the field into two quite distinct regions. At the right of the curve the vapor will be superheated or expanded. At the left it cannot exist, it is condensed, and there is nothing there except liquid. The ordinates of the curve show for each temperature the coexistence of the liquid and the vapor, that is, the state of saturation.

In the presence of a permanent gas, conditions are somewhat different. At the right of the curve the vapor is expanded and the gas is not saturated. Upon the curve the gas is saturated; at the left the gas is still saturated but there may exist some liquid not vaporized, however long the time of contact at constant temperature. This unvaporized liquid can only be completely vaporized by successively saturating new quantities of air with it. In other words, the temperature corresponding to an ordinate of the curve indicates the dew point of the body considered.

When we consider that it is necessary to vaporize the fuel completely before its introduction into the engine proper, it is seen that the quantity of air to be supplied depends not only on the chemical composition of the combustible under consideration, but also on the curve of vapor pressure and temperature. For liquids, the latent

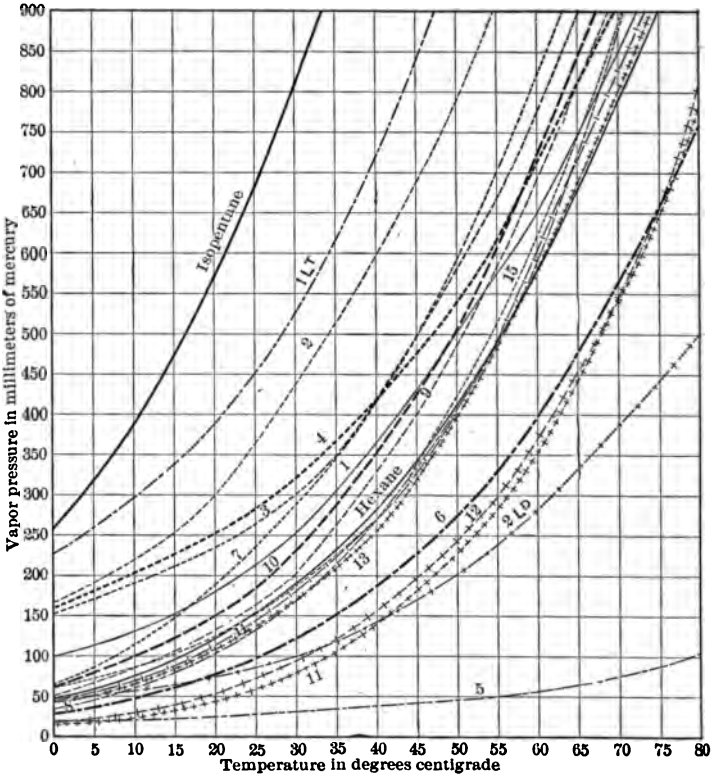


FIG. 18. VAPOR PRESSURE—TEMPERATURE CURVES FOR VARIOUS FUELS.

Isopentane.— Hexane.— *1*, Automobiline.— *1 LT*, Light portion of Automobiline. — *2*, Stelline.— *2 LD*, heavy portion of Stelline.— *3*, Motonaphtha. — *4*, Benzomoteur.— *5*, Coal oil.— *6*, Benzene. — *7*, Acetone. — *8*, Ninety per cent methyl alcohol. — *9*, Mixture of 75 per cent by volume of methyl alcohol, and 25 per cent of acetone (*A*). — *10*, Fifty per cent of methyl alcohol and 50 per cent of acetone. —*11*, Ninety per cent methyl alcohol. — *12*, Alcohol denatured by *9*. — *13*, Mixture of 75 per cent by volume of denatured alcohol and 25 per cent of benzene.— *14*, Fifty per cent denatured alcohol and 50 per cent benzene.—*15*, Twenty-nine per cent denatured alcohol and 71 per cent benzene.

heat of vaporization appears as a factor, since it lowers the temperature an amount directly in proportion to the latent heat of vaporization, unless an external source of heat is made use of.

Quantity of air theoretically necessary. — The quantity

of air theoretically necessary to secure complete combustion is shown by the following table, in which, as usual, alcohol is compared with the most common liquid fuels.

QUANTITY OF AIR REQUIRED FOR COMPLETE COMBUSTION.

Substance.	Chemical Symbol	Molecular Weight	Boiling Point.	Theoretic Volume of 1 Kilogram of Vapor.	1 Kilogram Requires		
					Oxygen.		Air.
			Degrees C	*Cu. Met.*	*Kilog.*	*Cu. Met.*	*Cu.Met.*
HYDROCARBONS OF THE METHANE SERIES.							
Pentane	C_5H_{12}	72	36	0.3100	3.555	2.4855	11.950
Hexane	C_6H_{14}	86	68.5	0.2595	3.535	2.4715	11.858
Heptane	C_7H_{16}	100	98	0.2232	3.520	2.4610	11.832
Octane	C_8H_{18}	114	125	0.1957	3.508	2.4529	11.795
Nonane a . . .	C_9H_{20}	128	130	0.1744	3.500	2.4472	11.766
Decane	$C_{10}H_{22}$	142	161	0.1572	3.493	2.4422	11.741
Undecane. . . .	$C_{11}H_{24}$	156	194.5	0.1431	3.487	2.4380	11.721
Dodecane . . .	$C_{12}H_{26}$	170	214.5	0.1313	3.482	2.4345	11.704
Tredecane . . .	$C_{13}H_{28}$	184	234	0.1213	3.478	2.4317	11.691
Tetradecane . .	$C_{14}H_{30}$	198	252	0.1127	3.475	2.4295	11.681
Pentadecane . .	$C_{15}H_{32}$	212	270	0.1052	3.472	2.4275	11.671
Hexadecane. . .	$C_{16}H_{34}$	226	287	0.0988	3.468	2.4247	11.659
Heptadecane . .	$C_{17}H_{36}$	240	303	0.0930	3.466	2.4233	11.650
Octodecane . . .	$C_{18}H_{38}$	254	317	0.0878	3.464	2.4219	11.644
BENZENE HYDROCARBONS.							
Benzene	C_6H_6	78	80.4	0.2862	3.077	2.1514	10.343
Toluene	C_7H_8	92	111	0.2426	3.130	2.1883	10.521
Xylene	C_8H_{10}	106	137	0.2105	3.169	2.2156	10.652
ALCOHOLS AND DERIVATIVES.							
Methyl alcohol .	CH_4O	32	64.5	0.6975	1.500	1.0489	5.042
Ethyl alcohol . .	C_2H_6O	46	78.4	0.4852	2.087	1.4591	7.015
Acetone	C_3H_6O	58	56.4	0.3848	2.207	1.5430	7.419
MIXTURES.							
1 liter of 90 per cent methyl alcohol weighs 0.8339 kilogram and contains:							
0.71965 kilogram	CH_4O	...	...	0.5019	0.6429	...	3.628
0.11424 kilogram	H_2O	...	...	0.1410			
For 1 kilogram .	...	...	...	...	0.7709	...	4.346
1 liter of methyl alcohol and acetone, mixture (A):							
0.750 liters of 90 per cent methyl alcohol = 0.6254 kilograms . .				0.8269	0.4822	0.5600	2.712	4.207
0.250 liters of acetone = 0.2015 kilograms					0.0778		1.495	
For 1 kilogram				...	...	0.6893	...	5.100

QUANTITY OF AIR REQUIRED FOR COMPLETE COMBUSTION.—*Continued.*

MIXTURES. — *Continued.* 1 liter of 90 per cent ethyl alcohol weighs 0.8337 kilogram and contains:				
0.71065 kilogram C_2H_6O	0.3448	0.4969	...	4.985
0.12327 kilogram H_2O	0.1521			
For 1 kilogram		0.5959	...	5.997
1 kilogram of alcohol denatured with (A) = 1.200 liters		0.6173	...	5.942
1 kilogram of carburated alcohol denatured with (A) = 1.171 litres		0.3953	...	8.218

Temperature theoretically necessary for vaporization.—The figures in the preceding table show that the vapors of the various substances considered are much expanded when mixed even with only the volume of air theoretically necessary for their combustion. Hence, there may be applied with a close approximation the laws of Mariotte and Gay-Lussac, assuming that the vapors have the densities theoretically due to their molecular weight.

If V = the volume of air in cubic meters necessary for the combustion of one kilogram of the fuel at 0° and 760 mm.

t = the temperature of the mixture of air and vapor.

x = the vapor pressure corresponding to that temperature.

d = the density of the vapor at 0° and 760 mm.

Then, since volume times density equals weight,

$$V(1 + a\,t)\frac{760}{760 - x}\,d\,\frac{x}{760}\,\frac{1}{1 + at} = 1$$

or,

$$\frac{x}{760 - x} = \frac{1}{Vd},$$

from which,

$$x = \frac{760}{1 + Vd}.$$

The following table gives the values of d, V, and x, for the substances previously considered.

	d	V	x
	Kilog. per cu. meter.	*cu. meters.*	
Pentane	3.225	11.950	19.2
Hexane	3.877	11.858	16.2
Heptane	4.481	11.832	14.1
Octane	5.110	11.795	12.5
Nonane α	5.734	11.766	11.1
Decane	6.361	11.741	10.0
Undecane	6.988	11.721	9.2
Dodecane	7.616	11.704	8.4
Tredecane	8.244	11.691	7.8
Tetradecane	8.853	11.681	7.2
Pentadecane	9.505	11.671	6.7
Hexadecane	10.121	11.657	6.4
Heptadecane	10.754	11.650	6.0
Octodecane	11.389	11.644	5.6
Benzene	3.494	10.343	20.4
Toluene	4.122	10.521	17.1
Xylene	4.751	10.652	14.7
Methyl alcohol	1.433	5.042	92.3
Ethyl alcohol	2.061	7.015	49.2
Acetone	2.599	7.419	37.5
90 per cent ethyl alcohol	1.678	5.997	68.77
90 per cent alcohol denatured by (A)	1.620	5.942	71.50
Alcohol carburated to 50 per cent	2.530	8.218	34.8

If there is found on any vapor pressure curve (Fig. 18) the point which has for its ordinate the value of x given in the accompanying table, the abscissa of this point gives the minimum temperature which the saturated mixture must have after complete vaporization.

Rapidity of evaporation. — It is still necessary that the time of contact should be sufficient to permit the evaporation which is, evidently, not absolutely instantaneous. But the time of contact during which vaporization must

take place is very short. A light high speed motor makes from 1500 to 1800 revolutions per minute. A heavy and consequently slow engine makes from 180 to 250. As the engines are usually 4-cycle, and a cycle corresponds to one half a revolution, it follows that the time of carbureting varies between $\frac{1}{60}$ and $\frac{1}{6}$ of a second.

Assuming, as a rough approximation, the approximate but simple law of August which serves for the graduation of his psychrometer, $\frac{dp}{dt} = k\,(P - p)$, in which $\frac{dp}{dt}$ is velocity of vaporization of a given liquid, k, a constant, P, the maximum vapor pressure corresponding to the temperature of the liquid, and p, the actual vapor pressure in the surrounding medium. Then, integrating from o to p,

$$t = \frac{1}{k} \text{ natural } \log \frac{P}{P - p}\,.$$

Saturation, then, cannot be quickly produced, for t would become, if not infinite, at least very large. But evaporation may be hastened either by raising the temperature through using the heat of the exhaust, or by introducing an excess of air, or by both means together.

The value of k is unknown, but the variation of log $\frac{P}{P - p}$ may be calculated for various fuels submitted to different temperatures and in the presence of variable quantities of air. Thus, the following table is obtained in which p is the value of the vapor pressure in the explosive mixture.

VALUES OF LOG $\frac{P}{P-p}$.

Ratio of Quantity of Air Used to Quantity Theoretically Necessary.	Values of p,	Hexane. Temperature in Degrees Centigrade. 60	50	40	30	20	10	0
	millim.	P=567mm	P=401mm	P=276mm	P=184mm	P=119mm	P=74mm	P=45mm
1.0	16.2	0.01259	0.01790	0.02627	0.04003	0.06356	0.10730	0.19382
1.1	14.7	0.01140	0.01622	0.02377	0.03616	0.05727	0.09618	0.17177
1.3	12.50	0.00968	0.01375	0.02013	0.03056	0.04820	0.08354	0.14133
1.5	10.8	0.00835	0.01185	0.01734	0.02627	0.04132	0.06851	0.11918
1.7	9.6	0.07441	0.01052	0.01052	0.02327	0.03653	0.06034	0.10421
		Benzene						
		P=390mm	P=271mm	P=188mm	P=120mm	P=77mm	P=45mm	P=27mm
1.0	20.4	0.02333	0.03399	0.04989	0.08092	0.13367	0.26227	0.61182
1.1	18.6	0.02122	0.03088	0.04525	0.07314	0.12008	0.22996	0.50708
1.3	15.8	0.01796	0.02609	0.03813	0.06131	0.09974	0.18783	0.38214
1.5	13.8	0.01564	0.02270	0.03311	0.05306	0.08577	0.15906	0.31079
1.7	12.2	0.01380	0.01997	0.02914	0.04657	0.07491	0.13734	0.26110
		Denatured Alcohol.						
		P=363mm	P=238mm	P=151mm	P=92mm	P=51mm	P=27mm	P=15mm
1.0	71.50	0.09527	0.15517	0.27861	0.66276	∞	∞	∞
1.1	65.58	0.08654	0.13999	0.24742	0.54186	∞	∞	∞
1.3	56.21	0.07306	0.11701	0.20222	0.41003	∞	∞	∞
1.5	49.22	0.06329	0.10063	0.17132	0.30255	1.45714	∞	∞
1.7	43.78	0.05582	0.08829	0.14871	0.28054	0.84903	∞	∞
		Denatured Alcohol Carburated to 50 Per Cent.						
		P=590mm	P=403mm	P=262mm	P=177mm	P=106mm	P=69mm	P=43mm
1.0	34.8	0.02640	0.03923	0.06189	0.09507	0.17283	0.30482	0.71066
1.1	31.8	0.02406	0.03570	0.05619	0.08600	0.15491	0.26831	0.58425
1.3	27.1	0.02042	0.03024	0.04742	0.07217	0.12823	0.21864	0.43207
1.5	23.6	0.11773	0.02621	0.04097	0.06214	0.10938	0.18179	0.34567
1.7	20.9	0.01566	0.02313	0.03610	0.05457	0.09538	0.15670	0.28908

It is evident from the table that two fuels presenting almost exactly the same vapor tension curves, such as hexane and French denatured alcohol mixed with an equal

volume of benzene, still act very differently in a carbureter in respect to the speed of vaporization. Thus, other conditions being equal, it is necessary to heat the carburated alcohol to 60° C. in order to vaporize it as rapidly as hexane heated to 40°; the temperatures, respectively, of 40° and 20°, 28° and 10°, 18° and 0°, correspond practically to the same rapidity of evaporation of these two liquids.

For denatured alcohol it is necessary that the temperature of the gaseous mixture should be 60° C. to obtain a velocity of evaporation equal to that of hexane at 11°.

VAPOR PRESSURES IN MILLIMETERS OF MERCURY.

Temperatures.	Hexane.	Alcohol Carburated to 50 Per Cent.	Benzene.	Denatured Alcohol.
−30	7	...	...	...
−29	7.5	...	...	...
−28	8	...	...	...
−27	8.5(1.7)	...	...	...
−26	9	...	...	...
−25	10 (1.5)	...	...	...
−24	11	...	...	...
−23	11.5	...	...	...
−22	12.5(1.3)	...	...	...
−21	13	...	...	...
−20	14	...	...	...
−19	15	...	7.5	...
−18	16 (1.1)	...	8	...
−17	17	...	9	...
−16	18.5(1)	...	9.5	...
−15	19.5	...	10.5	...
−14	20.5	19.5	11	...
−13	22	20.5(1.7)	12 (1.7)	...
−12	23	22	12.5(1.5)	...
−11	25	23	13.5	...
−10	26.5	24.5(1.5)	14.5	...
− 9	28	26	15.5(1.3)	...
− 8	30	27.5(1.3)	16.5	...
− 7	31.5	29	17.5	...
− 6	33.5	31 (1.1)	18.5(1.1)	11.5
− 5	35	32.5	20 (1)	12
− 4	37	35 (1)	21.5	12.5
− 3	39	37	22.5	13
− 2	41	38.5	24	13.5
− 1	43	41	25.5	14.5

When the temperature falls below 20°, the denatured alcohol practically cannot be entirely vaporized under the working conditions of the engine.

Herein lies the explanation of the necessity for heating the carbureter and one of the reasons for magnifying the quantity of air necessary. The excess of air ought to be larger in proportion as the volatility of the fuel is less, as the surface for transmitting heat is smaller and as the time of contact is shorter.

This need of an excess of air is a necessary evil in all

VAPOR PRESSURES IN MILLIMETERS OF MERCURY.

Temperatures.	Hexane.	Alcohol Carburated to 50 Per Cent.	Benzene.	Denatured Alcohol.
0	45	43	27	15
1	48.5	45	28.5	16
2	50	48	32	17
3	53.5	50	30	18
4	58	52.5	33.5	19
5	61.5	55	35.5	20
6	64	57.5	37	21.5
7	67	60.5	39	23
8	71	63	41.5	24.5
9	74	66.5	43.5	26
10	78	70	45.5	27.5
11	82.5	72.5	48.5	29
12	87	75.5	51.5	31
13	90	79	54	33
14	95	82.5	57	35
15	99	86	60.5	37
16	103	90	63.5	39.5
17	108	93.5	67	42
18	113	97.5	70.5	45 (1.7)
19	118.5	112	74	48
20	124.5	106.5	77.5	51 (1.5)
21	131	111.5	81	54
22	137.5	117.5	85	57.5(1.3)
23	145	123.5	88.5	61
24	...	130	92.5	64 (1.1)
25	...	136.6	90.5	68 (1.1)
26	...	145	100.5	72 (1)
27	...	...	105	76.5
28	...	...	110	81
29	...	...	115	86
30	...	...	120	92

explosion engines using liquid fuel. Evidently the excess of air lowers the temperature of combustion and diminishes correspondingly the maximum pressure obtained, while also the exhaust gases carry away a greater quantity of heat.

Influence of the quantity of air on the necessary temperature. — In the table on pages 148 and 149 are given the pressures which the vapors of hexane, benzene, denatured alcohol, and carburated alcohol have for saturation at various temperatures. At the same time, the figures in parentheses show the ratio of air present to the amount of air theoretically necessary for the complete combustion of the fuel vapor present.

Again it appears from this comparison, that there are marked differences between the use of the gasolines, of which hexane is the type, and carburated denatured alcohol, although the vapor pressure curves almost coincide. Hexane is able to give a satisfactory explosive mixture at low temperatures, while at the same temperatures it is impossible to secure the satisfactory operation of an engine on carburated alcohol, and hence much less on denatured alcohol.

From this arises the necessity encountered by makers of alcohol engines, either for heating the carbureter before starting or for using gasoline for a time until the exhaust is able to heat the carbureter sufficiently to produce satisfactory vaporization. Some makers, who use an incandescent tube for ignition, heat the sprayed mixture with the waste heat from the burner. But without special care the velocity through the heaters is too great to make sure of complete vaporization.

Quantity of heat absorbed in vaporization. — In order to secure complete vaporization it is necessary not only to raise the air and vapor to the temperature given above,

but also to supply the quantity of heat necessary to convert the liquid into vapor, quite another matter.

Consider first the lighter petroleum oils which may be considered calorifically to consist of hexane, whose specific heat is 0.50 and whose latent heat of vaporization is 117 calories. It is necessary to supply these 117 calories either at the expense of the ingredients of the mixture or from an external source.

If we use the theoretical quantity of air, that is, 15.337 kilograms per kilogram of hexane, the mixture of liquid and air is capable of supplying heat for 1 degree fall of temperature as follows:

Hexane	0.500
Air, 15.337×0.2375	3.642
Total	4.142

The quotient, $\frac{117}{4.142} = 28.04$, gives the minimum initial temperature which ought to be added to that obtained for the point of saturation in order that complete vaporization may be possible.

The lowest temperature for saturation has previously been found to be $-17.2°$ C. Hence, complete vaporization would be possible only if the initial temperature of the air and hexane is higher than $-17.2 + 28.04 = 10.84°$. It ought to be higher in proportion to the speed of the motor.

If 1.3 times the theoretical amount of air is used, or 19.938 kilograms per kilogram of hexane, the minimum temperature for complete vaporization is $-24°$ C. The heat capacity of the air and hexane is,

Hexane	0.500
Air, $19.938 \times 0.2375 =$	4.735
	5.235

and the minimum initial temperature is $-24 + \frac{117}{5.235} = -1.7°$ C.

Finally, if 1.7 times the theoretical quantity of air is used, the critical temperature for total vaporization is $-27°$ and the minimum initial temperature is $-10°$.

Naturally, as explained previously, the minimum initial temperature ought to be raised above the figures indicated, in proportion as the speed of the motor increases and the quantity of air is more limited.

Taking up alcohol denatured with mixture (*A*), as a type of all industrial alcohols, it contains per kilogram:

90 per cent ethyl alcohol	0.9098 kilograms
90 per cent methyl alcohol	0.0682
Acetone	0.0210
	.9990

or,

$0.9098 \times 0.857 =$	$0.7797\ C_2H_6O$
$0.0682 \times 0.842 =$	$0.0574\ C\ H_4O$
	$0.0210\ C_3H_6O$
	$0.1419\ H_2O$
	1.0000.

According to Regnault, the heats of vaporization near 20° C, are,

Anhydrous ethyl alcohol	$252 - 11.4 = 240.6$
Anhydrous methyl alcohol	$267 - 12.6 = 254.4$
Acetone	137.3
Water	592.0

Hence the vaporization of 1 kilogram of the mixture requires,

$$\begin{aligned} 240.6 \times 0.7797 &= 187.59 \text{ calories.} \\ 254.4 \times 0.0574 &= 14.60 \\ 137.3 \times 0.0210 &= 2.88 \\ 592. \times 0.1419 &= 83.41 \\ \hline & 288.48 \text{ calories.} \end{aligned}$$

The specific heat of 90 per cent ethyl alcohol around 20° C is 0.791, of 90 per cent methyl alcohol it is 0.680, of acetone, 0.501. If there is employed the quantity of air exactly necessary, or 7.685 kilograms per kilogram of the fuel, the heat capacity of the air and liquid is,

90 per cent ethyl alcohol	0.791	× 0.9098	= 0.7196	0.7764
90 per cent methyl alcohol	0.680	× 0.0682	= 0.0463	
Acetone	0.501	× 0.0210	= 0.0105	
Air	0.2375	× 7.685	= 1.8252	
			2.6016	

The critical temperature for complete vaporization being 25.8° C, the minimum initial temperature of the mixture ought to be

$$25.8 + \frac{288.48}{2.6016} = 136.68° \text{ C.}$$

Hence complete vaporization without the use of external heat is entirely out of the question. Similarly, supposing that 1.7 times the theoretical quantity of air is used, having a thermal capacity for the mixture of 3.8791, and having as a critical temperature for complete vaporization 17.5° C, the minimum initial temperature is still 91.87° C.

If an attempt is made to start the engine at 15° C. without using external heat, assuming that the carbureter has a thermal capacity equivalent to 0.5 kilogram of water and that 1.7 times the theoretical quantity of air is used, there will be a great cooling due to the vaporization, a cooling which will be greater the longer the fuel stays within the carbureter.

If T = final temperature, and x = the quantity vaporized, $[1 \times 0.7764 + 7.685 \times 1.7 \times 0.2375 + 0.5]\ 15 = x \times 288.48 + [(1 - x)0.7764 + 7.685 \times 1.7 \times 0.2375 + 0.5]\ T$.

$$x = \frac{[0.7764 + 7.685 \times 1.7 \times 0.2375 + 0.5]\ (15 - T)}{288.48 - 0.7764\ T}$$

$$= \frac{4.3791\ (15 - T)}{288.48 - 0.7764\ T},$$ the equation of an equilateral hyperbola.

We find, for	$T = 15°$ C	$x = 0.000$
	10	.078
	5	.154
	0	.227
	5	.297

Hence, only a very slight quantity of denatured alcohol would be vaporized (probably the more volatile portions would distil off). The remainder would be drawn along as fog, part would adhere to the admission valve, where after the first explosion (if one were able to take place) it would undergo a series of complex decompositions. Another part would collect on the cold walls of the cylinder and would be only partially vaporized during the explosion, forming then a heterogeneous mixture of combustible vapors and gaseous products of combustion partly deprived

of air. From this would appear black smoke charged with formaldehyde and acids. These are produced during the first explosions, if the motor starts at all, as well as tar-like deposits which form on the exterior of the admission valve, until the exhaust gases are able to supply the needed heat.

A carbureter may be imagined which would be satisfactory for gasoline but very unsatisfactory for denatured alcohol because it is unable under normal operation to transmit the needed quantity of heat.

Sometimes, instead of heating the whole mixture of air and combustible, the air only is heated. Supposing 1.7 times the necessary quantity of air is used, or 13.064 kilograms per kilogram of denatured alcohol, a fall in temperature of the air of 1° C. will furnish 3.1027 calories. It is necessary, then, to heat the air above the critical temperature at least $\frac{288.48}{3.1027} = 92.9°$ C.

Knowing the slowness with which heat is transmitted between gases through a metallic wall, it is apparent that it is necessary to give a large area to the wall, which has been found to entail serious difficulties when the contact takes place in the exhaust pot.

Taking up lastly carburated alcohol, only the 50 per cent mixture, the one chiefly employed, will be considered. 1 kilogram of the mixture contains,

Alcohol denatured by (A) .	0.486 kilograms
Benzene	0.515

The heat of vaporization is,

Denatured alcohol	$0.486 \times 228.48 =$	140.201 calories
Benzene	$0.515 \times 109 =$	56.135
		196.336

The specific heat is,

Denatured alcohol	$0.486 \times 0.7764 =$	0.377
Benzene	$0.515 \times 0.4359 =$	0.224
		0.601

If the theoretical amount of air is used, 10.629 kilograms per kilogram of the fuel, corresponding to a critical temperature of $-4.2°$ C, the mixture will have a specific heat of:

Carburated alcohol . . .	0.601
Air, $10.629 \times 0.2375 =$	2.524
	3.125

and it is necessary that the initial temperature be higher than $-4.2 + \frac{196.336}{3.125} = 58.5°$ C.

Hence, already the conditions are much improved. When 1.7 times the theoretical quantity of air is used, the calorific capacity of the mixture becomes,

Carburated alcohol . . .	0.601
Air, $18.169 \times 0.2375 =$	4.315
	4.916

and the critical temperature is $-14.8°$ C.

Hence the minimum initial temperature is $-14.8 + \frac{196.336}{4.916} = 25.9°$ C.

Hence little is lacking to secure complete vaporization. If the engine is started at a temperature of 15° C, there is available a fall of temperature of $15 - (-14.8) = 29.8°$, which is able to supply $4.916 \times 29.8 = 146.496$ calories, permitting the vaporization of $\frac{146.496}{196.336} = 74.61$ per cent of the fuel. Hence there will still be the forma-

tion of smoke in starting, but much less than in the case of denatured alcohol.

In what precedes it has been supposed that the air and fuel are mixed at the same temperature and are heated simultaneously. Evidently a smaller carbureter may be used if only a part of the air is heated with the fuel and then the remainder of the air is injected into the superheated mixture, provided that the temperature of the mixture remains appreciably above the initial minimum temperature calculated.

But it is wholly bad to heat the fuel by means of the exhaust before mixing the fuel with air. The fuel would distil between two consecutive suctions and give a mixture whose composition it would be impossible to regulate. There was a very clear example of this defect at the French competition of November, 1901.

Very clearly, it is a mistake to suppose that a carbureter suited to the lighter petroleum oils is suited to alcohol more or less carburated with benzene.

But, on the other hand, a carbureter suited to alcohol may also be used for gasoline. A carbureter vaporizing completely heavy coal oil, for example, will be suitable for the more volatile products, under some restrictions which will be considered later in this book.

Influence of the temperature of the cylinder walls. — According to what precedes, the starting of an engine on carburated alcohol is necessarily accompanied by incomplete combustion. It is the same, of course, with denatured alcohol until the heat furnished by the exhaust to the walls of the carbureter is able to raise the explosive mixture to such a temperature that all the fuel is vaporized and mixed uniformly with the air supplied.

Another cause of poor combustion in starting is the temperature of the cylinder walls. At first this temper-

atûre is the same as the jacket water, about 15° or 20° C. The walls are, therefore, incapable of warming up the entering gas, which on account of the slight opening of the admission valves suffers an appreciable expansion in passing from the carbureter into the cylinder.

Let P_0 = the pressure of the gas before entering the cylinder, P_1 = the pressure in the cylinder during suction stroke, T_0 and T_1 the corresponding absolute temperatures. Considering the expanded vapors as perfect gases,

$$\frac{T_1}{T_0} = \left(\frac{P_1}{P_0}\right)^{0.4}.$$

The ratio, $\frac{P_1}{P_0} = n$, will decrease as the speed of the engine increases and as the valve opening is less. Giving T_0 the value $274 + 10 = 284$, P_0 the value 1, we get the following results for different values of n:

n = 0.99	t = 8.8° C
.97	6.5
.95	4.3
.925	1.3
.90	− 1.7
.85	− 7.8
.80	− 14.2

Evidently, since the cylinder walls are cold, they cannot, on account of the quickness of the phenomenon, rapidly enough restore sufficient heat to compensate for this cooling. Plainly, it is desirable to diminish the fall in pressure during the suction stroke. This difficulty cannot be overcome by increasing the lift of the valve on account of the shock of its reseating, but it may be diminished by increasing the diameter of the valve.

A notable improvement of this sort was obtained in an automobile engine working on alcohol.

CHAPTER VIII.

INVESTIGATIONS ON CARBURETERS.

Disadvantages of flow through capillary orifices. — It has long been known that temperature greatly influences the viscosity of liquids, and that, consequently, with any given liquid, a greater flow will take place through a capillary tube, as the temperature is raised. Hence if the fuel reservoir and the carbureter are near enough to the motor to be heated by its radiation, such a type of apparatus, well regulated on starting, will furnish a charge more and more rich the longer it runs, and the combustion will become less and less perfect.

There being no detailed researches on the viscosity of the liquids and their mixtures under investigation, the author undertook a series of experiments, including not only alcohol mixtures but also gasoline and the heavier petroleum oils used in explosion engines.

The apparatus adopted appeared to be preferable to that employed by Poiseuille in his classic experiments. As in his experiments the capillary glass tube used was carefully cleaned with nitric acid, soda, concentrated alcohol, then with water, and was well dried in a current of filtered air.

Contrary to the method of Poiseuille, the author compared not the volumes but the weights that ran through in a given time, since in all mechanical or calorimetric measurements it is the weight which is used. Moreover, the author worked under a constant pressure, and not as Poiseuille, under a slightly varying pressure.

Let D = amount flowing through the capillary tube per unit of time;

H = pressure head on the liquid;
d = diameter of tube;
l = length of tube;
k = a constant coefficient.

The law announced by Poiseuille and represented by the equation, $D = k\frac{Hd^4}{l}$, was established for wet capillary tubes in which the length was very great compared with the cross section. Poiseuille showed in addition that if the length becomes comparable to the section, H would be affected with an exponent larger than unity.

Since for the purposes under consideration only short capillary slits or capillary orifices are used, the simple law of Poiseuille is not applicable, because H must have some unknown exponent. But it is only necessary to investigate the coefficient, k. In order to have a standard of comparison, all the results have been compared with those furnished by distilled water at 15° C.

To magnify the differences in the value of k, the head of liquid used was reduced to a very small value, 30 millimeters, and a considerable length, 49 centimeters, was given to the capillary tube. A tube of very uniform bore was selected whose average diameter was 0.775 millimeters.

Fig. 19 illustrates the apparatus used. The liquid was contained in a 500 cubic centimeter bottle having a lateral opening near the bottom and provided with a Mariotte tube, *a b*. This tube reaches to the bottom of the bottle and is fastened to the outlet tube, *c d*, in such a way as to have a constant position during each experiment. At

a point, A, is blown an opening, sharply notched, by which air is admitted. Thus, the entrance of air is very regular and does not produce in the tube oscillations greater than one millimeter.

The capillary tube, $d\ e\ f$, is entirely immersed in a bath kept at a constant temperature by a good Schloesing thermo-regulator. One end of the capillary tube is fastened to a stopcock tube, $c\ R\ d$, whose interior diameter is about four millimeters and whose influence may be neglected since the ratio $\frac{D^4}{d^4} = 427$. The other end of the capillary tube is connected to an overflow, $f\ g$, provided at its highest point, B, with an orifice that prevents any siphoning in the overflow. When the flow is once established, the meniscus, $m'\ n'$, remains of absolutely constant form and the liquid runs freely the length of the wet walls.

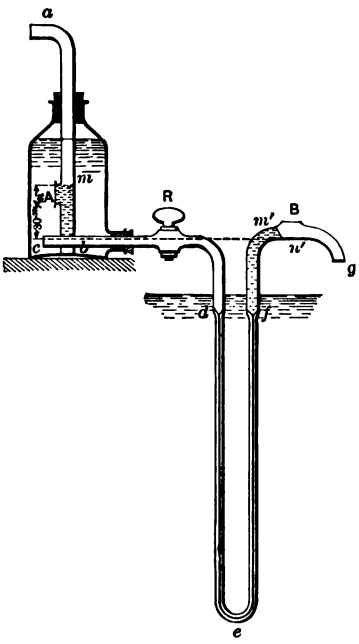


FIG. 19. FLOW THROUGH A CAPILLARY TUBE.

The temperature of the bath having been regulated, the Mariotte bottle and the tube, $c\ g$, were rinsed with the liquid to be studied, the Mariotte bottle was filled with the liquid, all the air was driven from the outlet tube and the cock, R, was opened until the level of the liquid in the Mariotte tube was brought to the level, m. Then the cock, R, was closed and the apparatus was quickly weighed

on a Roberval balance sensitive to 0.5 gram. It was arranged over the bath so that the capillary tube was completely submerged. The end, g, was loosely inserted through a cork in a vessel dipping into the bath so that there should take place neither condensation of water from the atmosphere nor evaporation in the part, $n' g$.

The time of opening the cock, R, was noted. At the expiration of a suitable time, which varied from 80 to 120 minutes, the cock was closed, the apparatus was carefully dried and again weighed. The loss of weight, representing the quantity which had run out in the measured time, was reduced to flow per hundred minutes.

For each substance studied, the results just as calculated were plotted on a diagram, using temperature for abscissas and the quantity flowing out in 100 minutes for ordinates. The points thus established were joined by a smooth curve and the variations in no case exceeded the possible experimental error of 1 gram.

The same maximum temperature could not be used for all the substances, for it was necessary to avoid the formation of gaseous bubbles in the capillary tube, since this would have produced relatively enormous errors in the results.

Although the interior diameter of the capillary tube varies with the temperature, this source of error is negligible in this kind of experiment, for using the customary coefficient of expansion for ordinary glass, the ratio

$$\left(\frac{d \text{ at } 60^\circ \text{ C}}{d \text{ at } 10^\circ \text{ C}}\right)^4$$

does not exceed 1.03.

The following table gives the results obtained from the diagram:

THE WEIGHT OF VARIOUS LIQUIDS FLOWING THROUGH A CAPILLARY TUBE IN ONE HUNDRED MINUTES, UNDER THE PRESSURE OF 30 MILLIMETERS OF THE SAME LIQUID.

Substance.	Temperatures Centigrade.											
	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.
1. Water	...	42	80	91	101.5	115	129.5	140	153.7	167	181	195.5
2. Pure 90 per cent alcohol	...	14.6	17.7	20.2	21.5	25	28	33	39.5	46	52.5	60
3. French denatured alcohol	17.5	19.7	22.3	25.3	28.3	30.2	33.3	36.5	40.5	45.3	50.0	54.5
4. Pure benzene*	49.3	56	62.3	68.6	75.6	82	87.6	92.5	97	102.5	108	113.5
5. 50 per cent denatured alcohol, and 50 per cent crystallizable benzene	30	34.6	39.3	44.2	49	53.5	58.5	64.2	71.7	82	97	
Specific gravity — *boiling at*	Substances Extracted from American Petroleum.											
6. 0.700 — 12° to 134°	68	70.5	72.5	74	75.7	77	80	84	89.7	96.5	...	...
7. 0.725 — 70° to 134°	48.3	52.2	56	59.8	63.3	66.3	69.7	73	76.7	80.2	...	...
8. 0.755 — 125° to 196°	39.8	41.5	42.5	44.7	47.8	51.5	54.5	58	61.7	65.7	70.3	76.5
9. 0.788 — 196° to 250°	16.5	19.6	21.5	25.2	28	31	34	36.5	39.5	42.2	45	48
10. 0.817 — 250° to 310°	7.5	8.6	10.2	11.7	13	14.3	15.9	17.5	19.2	21	23	25

* Very slight amounts of impurity suffice to change the internal friction of the liquid very materially and in an irregular manner. Thus, it was found:

Temperatures.	45°	50°	55°	60°	65°	70°
	gr.	gr.	gr.	gr.	gr.	gr.
Pure benzene	97	102.5	108	113.5	119.2	125
Commercial crystallizable benzene	97	102.8	111.2	122.8	128.5	130.4

It is necessary to reduce the experimental results to a uniform pressure. Assuming, according to Poiseuille and Dubuat, that the discharge through long * capillary tubes is proportional to the head and not to its square root, as in the case of orifices in thin walls, we are able to deduce from the preceding results the relative discharges under a constant pressure of 30 millimeters of distilled water at 15° C.

This standard was chosen, first, because it corresponds to one of the experimental values, and, second, it is sufficient to give a velocity of 21.30 meters per second to the air in the suction pipe of a carbureter, a velocity comparable with that of the vapor in the pipes of good engines.

The table on page 165 and Fig. 20 show the results of this calculation.

The lines thus obtained do not have the appearance of geometrical curves. They are mostly lines with a long reverse, of which the semi-straight portion joins two parts more curved, one of which corresponds to temperatures near the temperature of crystallization or of maximum density, and the other corresponds to temperatures near the boiling point, especially in the case of complex mixtures.

* According to Poiseuille, the discharge increases faster than the pressure unless the ratio of the length to the diameter equals a large definite value.

RELATIVE WEIGHTS OF DIFFERENT LIQUIDS FLOWING UNDER THE SAME PRESSURE THROUGH THE SAME CAPILLARY TUBE IN THE SAME TIME, COMPARED WITH DISTILLED WATER AT 15° C.

Substance.	Temperatures Centigrade.											
	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.	gr.
1. Water		52.5	100	115	129	144	159.7	175	195	211	...	...
2. Pure 90 per cent alcohol	14.5	21	26.5	29.7	32.5	36.5	42.5	50	59.5	69.5	80	93
3. French denatured alcohol	26.2	29.7	33.7	37.7	41.5	45.5	49.7	54.5	59.5	67	74.5	81.5
4. Pure benzene	70.2	79.5	88.5	98	107	115	123	130	137	143.8	152.7	160.5
5. 50 per cent denatured alcohol and 50 per cent crystallizable benzene	43.5	50.5	57.5	62.3	71.3	78.2	85.3	94	105	119.5	142	...
Specific gravity — *boiling at* — Products Obtained from American Petroleum.												
6. 0.700 — 12° to 134°	121.5	125.5	128.5	131.5	134.5	138	143.3	150	156.5	163	...	...
7. 0.725 — 70° to 134°	82.6	90	97.6	104	111	118	122.5	126.5	131	138	146	...
8. 0.755 — 125° to 196°	66	68.5	71.5	75	79.5	84.5	90.2	96	102.2	109	116.7	126.5
9. 0.788 — 196° to 250°	26.2	29	34.5	36.5	42	47	52.3	58	62.5	67.5	72	77
10. 0.817 — 250° to 310°	11.5	13	15.5	18.7	20	22	24.3	27	29.7	32.3	35.3	38

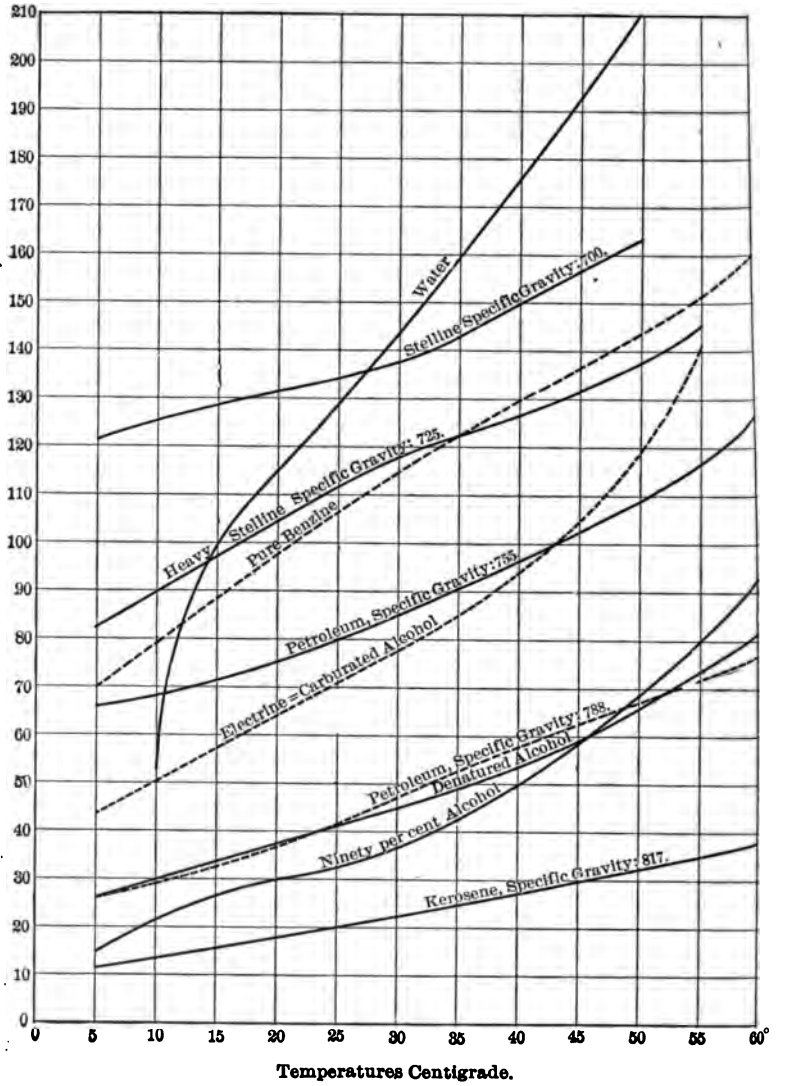


FIG. 20. FLOW OF VARIOUS LIQUIDS THROUGH A CAPILLARY TUBE UNDER CONSTANT PRESSURE.

The variations in discharge are often so rapid that the charging of the air by means of apparatus with capillary orifices cannot be expected to remain constant throughout a whole day. A satisfactory carbureting can only be hoped for by the use of an excess of air in such manner as to keep the average conditions about right and such that at no time during the whole day shall there occur a mixture containing an excess of combustible. It has been previously shown that the need of a rapid vaporization leads to the same conclusion. In the study of the various stationary alcohol engines entering into the international French competition in May, 1902, it was found that the best carbureting was accomplished when the mixture contained from 1.3 to 1.7 times the quantity of air theoretically required for complete combustion. Probably it is necessary to keep within these limits and to regulate the carbureter in such a way as always to be near the average ratio of 1.5.

Moreover, an inspection of the curves shows that the variations in discharge of the various fuels differ greatly as the temperatures change. Thus, as regards viscosity, the heavy petroleum oils present much smaller variations than alcohol, either pure, denatured, or carburated, and less than the lighter petroleum oils. According to this, with kerosene it ought to be possible to diminish the excess of air, and the figure 1.3 which Ringelmann obtained in his experiments seems very satisfactory.

The variations in discharge caused by heating the carbureter by radiation from the engine are considerable. What, then, should be thought of apparatus where the supply of the fuel is obtained by squirting and where the liquid is previously heated by the exhaust? In engines having a hit-and-miss governor and a spray carbureter in which the liquid is previously heated by the exhaust,

the temperature of the liquid before spraying will vary from one explosion to another, and hence the carbureting will be constantly changing.

The shape of the curves representing the relative discharges through the same capillary orifice, shows that when the temperature varies but little from the best value it might be possible without too great complications in stationary or portable engines to avoid, by a suitable regulation of the suction, one of the disadvantages of spraying. In short, if the viscosity of the liquid decreases as the temperature rises, too great a charge of fuel may be avoided by opening the admission for pure air in such a way as to diminish the fall of pressure during the suction stroke. On the other hand, the charge may be increased by closing the opening for admission of air.

But if only a comparatively small range of temperature of the fuel is considered, say 20 or 30 degrees above the average temperature of 15° C, inclined straight lines corresponding to the average flow may be practically substituted for the long curves.

Let W = weight of pure air drawn in.
T = temperature of the air.
S = cross section of air admission pipe.
P = fall of pressure.
w = weight of liquid drawn in.
t = temperature of liquid.

$$W(1 + aT) = KS\sqrt{P}.$$

And according to the law of Poiseuille,

$$w = K' Pf(t).$$

But, if the rate of charging is to be constant,

$$W = mw.$$

From which, eliminating w and P,

$$mW\,(1 + aT)^2 = \frac{K^2}{K'}\frac{S^2}{f(t)}.$$

If, for the very complex function, $f(t)$, we substitute in such a range of temperatures as will permit it, the linear function, $c + bt$, which sufficiently well represents the long flat reversed curve, we have,

$$S^2 = \text{constant} \times W(1 + aT)^2\,(c + bt).$$

Hence, in a shop where the temperature varies little during the period of operation, but where the radiation of the engine affects the temperature of the carbureter, the cross section for admission of air should vary proportionally to the binomial, $c + bt$.

Assuming the cross section to be rectangular: $S = ed$, e being constant and d variable. We have approximately,

$$d^2 = n(c + bt).$$

Hence, in addition to a governor actuated directly by the velocity or acceleration of the engine, it would be well, in the case of spray carbureters, to have a second governor operated by the temperature of the carbureter which will vary one of the dimensions of the rectangular orifice for admitting air, in accordance with the above equation.

Influence of cold on alcohol-benzene mixtures. — In addition to the effect of ordinary temperatures on the velocity of flow of liquid fuel, there should be noticed the effects of extreme cold, which is especially noticeable in spray carbureters.

Since commercial denatured alcohol is not a homogeneous substance, the author made a mixture of 100 volumes of 90 per cent ethyl alcohol, and 10 volumes of

a mixture of the same density at 15° C. composed of 75 parts of methyl alcohol to 25 parts of pure acetone.

To this was added various proportions of pure benzene and the whole was submitted to the action of cold.

Two cases can be distinguished.

In the first, a lowering of the temperature causes a separation of the liquid into two distinct layers, the upper consisting of alcohol saturated with benzene, and the lower of benzene saturated with alcohol.

In the second case, the benzene, the only body existing in the mixture capable of crystallization, separated out in the form of very fine crystals which turn all or part of the mass into a solid body interrupting the action of the carbureter.

Although two cases exist, the first has little practical interest, for it is observed only in mixtures richer in benzene than it is customary to use.

Thus, a mixture of 75 per cent pure benzene and 25 per cent of alcohol denatured as above is not stable at 20° C. It forms an emulsion and separates in a few moments into two distinct layers, of which the upper is the smaller.

The mixture of 70 per cent pure benzene and 30 per cent of the same alcohol separates at + 2° C. A mixture of 65 per cent pure benzene and 35 per cent of denatured alcohol separates at − 1° C. Beyond these proportions the division into two layers is no longer observed, but instead a separation of crystallized benzene. Below are some experimental results. It should constantly be noted that pure benzene presents in a high degree a tendency towards supersaturation and that it is difficult to duplicate results without either a prolonged agitation or introducing into the cold mixture a trace of crystallized benzene.

Mixture of 75 per cent benzene gives crystals at . . . . . – 4° C
Mixture of 70 per cent to 40 per cent benzene gives crystals at . . . . – 5°
Mixture of 40 per cent to 35 per cent benzene gives crystals at . . . . – 19°

This inconvenience may be avoided by substituting for the pure benzene the commercial mixture known as 90 per cent benzol, practically constituted of 84 per cent benzene, 15 per cent toluene and 1 per cent xylene. This mixture is almost as easily vaporized with denatured alcohol as pure benzene, but it has the property, due to the presence of toluene, of not solidifying until a much lower temperature.*

Thus, using denatured alcohol in a 50 per cent mixture with 90 per cent benzol the author found that the liquid became doubtful at – 14° C; at – 20° C the separation into two liquid layers was very distinct; at – 20.5°C there was solidification. The presence of toluene lowers, then, the critical temperature about 15°C. This is sufficient for practical purposes because the freezing of the water necessary for cooling the engine would have previously stopped its operation.

For various reasons, largely commercial, it has been proposed during the last few years to substitute for coal benzene the lighter petroleum oils, either as obtained direct from distillation or after the operation of *cracking*. These hydrocarbons are very slightly soluble in 90 per cent alcohol. They are more so in 95 per cent alcohol, but their solubility is greatly augmented by the addition of amyl alcohol. It is not sufficient for this purpose to employ

* Commercial impure benzene may even now be obtained which distils entirely at 100° C and which possesses practically the same advantage, while vaporizing more readily.

what is known commercially under the name of amyl oil and which is the residue from the rectification of alcohol. This product contains water, mixed ethers, and the various alcohols, propyl, butyl, amyl, caproic, etc. Such a mixture is a poor solvent and does not prevent separation from cold. On the contrary, with practically pure amyl alcohol rectified over quicklime, there can be added to 95 per cent alcohol an equal volume of a mixture composed of 14 per cent amyl alcohol and 86 per cent gasoline without there being separation or solidification at − 21° C.

Carbureting by surface evaporation. — In the preceding discussion it has been assumed that a definite weight of the liquid fuel was placed in the presence of an equally definite weight of air, under conditions suitable for complete vaporization.

But we have already seen that in the passageway of the air, which is more or less saturated with combustible vapor and charged with little drops of the fuel, there may be found in most spray carbureters either metallic gauze or diversion plates intended to retain and break up the tiny drops of liquid and to spread them over a large surface in contact with the air to secure their vaporization.

In other devices, much more rare, a constant level reservoir is furnished with wicks blown upon by the gaseous current. The latter is thus saturated and at the same time it draws along a small quantity of the liquid in the form of spray.

This method does not at all permit an automatically regulated mixture, and is, hence, imperfect when used with a homogeneous substance. Clearly, then, if the liquid is a mixture, there takes place on the metallic gauze or in the wicks a selective vaporization, vaporizing the lighter portions and leaving the less volatile parts. In the case of wicks, diffusion maintains a continuous exchange

between the liquid saturating them and that which fills the reservoir, such that the latter is gradually charged with the less volatile constituents and the residue becomes more and more unsuitable for carbureting.

Finally, a type of carbureter generally abandoned forces the air in a very thin layer over the surface of the liquid maintained at a constant level.

The experiments described below show that any carbureter will work badly in which an excess of a heterogeneous liquid fuel is exposed to a current of air.

Since many in practice have attributed the difficulties of this kind of carbureting to a condensation of water vapor and not to a selective vaporization, the author has avoided any doubt on this point by using air previously dried by a long column of calcium chloride.

To obtain contact of the air and liquid, two quite different methods were used. In one, the liquid to be studied trickled down in excess in the presence of dry air; in the other, the dry air was made to bubble through a known weight of the liquid to be studied, of such an amount that the level remained practically constant.

Carbureting by trickling. — The apparatus used is shown in Fig. 21. A tube, *ss*, was made of tin so as not to be corroded by the mixtures used within the temperatures of the experiment. The tube was 3 meters long, 13 millimeters in internal diameter, and was formed into a coil in a cylindrical vessel, *A*, filled with water which was kept at a constant temperature by a Schloesing thermo-regulator controlling the burner, *B*.

A Mariotte bottle, *C*, furnished with a cock, *r*, permitted the liquid to be studied to flow out, drop by drop, through the capillary siphon, *cc*, into the tube, *dd*, arranged to provide against the formation of a vacuum, and joined to the upper end of the coil, *ss*. The liquid moistens the interior

surface of the coil and quickly takes the temperature of the bath. A part is vaporized in the current of dry air and the excess runs off through the safety tube, *e*, and falls into

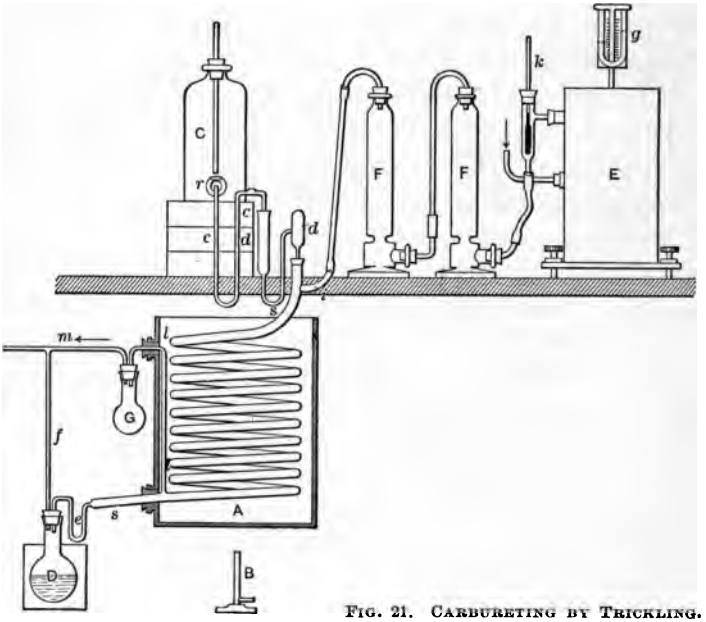


FIG. 21. CARBURETING BY TRICKLING.

the cold flask, *D*, from which the air escapes through the tube, *f*.

The necessary air was forced in by a water blower delivering 75 to 80 litres per hour. It was measured in a meter, *E*. A small water manometer, *g*, indicated the pressure at the outlet of the meter and a thermometer, *h*, entirely immersed in the gaseous current immediately beyond the outlet, showed its temperature.

The air was next dried by passing through two long tubes, *F*, *F*, filled with calcium chloride, and finally entered the coil by the lateral tube, *i*. The air passed through the whole coil in the same direction as the liquid and escaped

through the vertical tube, *ll*, immersed in the bath to prevent the return of any condensation to the residual liquid. Immediately after leaving the bath the tube, *ll*, enters a flask, *G*, which acts as a condenser. From there, the cooled gases pass out through the tube, *m*, connected to the tube *f*.

In all the subsequent calculations the air is reduced to 0° C, under its actual pressure. It is considered dry when it first comes in contact with the liquid fuel.

Let V = the volume shown by the meter,
H = the atmospheric pressure,
h = the pressure in millimeters of mercury indicated by the manometer, *g*;
t = the temperature of the gas when it leaves the meter;
f = the maximum pressure of water vapor corresponding to the temperature, t;
V_0 = the volume of dry air reduced to 0° C, under a pressure, H, corresponding to the volume, V, shown by the meter dial.

$$V_0 = V \frac{H + h - f}{(H + h)(1 + at)}.$$

The bath was raised to the desired temperature, the contents of the flask, *C*, was run into the coil to wet its interior surface, and the pump was started. In a short time, when a steady state had been reached, the Mariotte bottle, *C*, and the flask, *D*, were quickly weighed. When the reading of the meter was exactly a whole number, the cock, *r*, was opened, and simultaneously the flask, *D*, was put under the outlet tube. The barometric pressure, *H*, the pressure, *h*, shown by the water manometer, *g*, and the temperature of the gas shown by the thermometer, *k*, were all recorded.

At the end of an hour and a half or two hours, the same observations were repeated and when the reading of the meter was exactly a whole number the cock, r, was closed, and the flask, d, was quickly removed.

From the weight of the Mariotte bottle, C, was obtained the weight of liquid that had run out during the experiment. From the weight of the flask, D, was obtained the weight of the liquid not vaporized. The difference was the weight of liquid vaporized at a known temperature and in a volume of air easily calculated. Thus, the weight vaporized by 100 litres of dry air was easily obtained.

In the case of simple mixtures like water and alcohol, the specific gravities at a temperature of 15° C. showed the composition of the initial mixture and of the residual mixture. From this the weight and the composition of the portion vaporized could be obtained.

With denatured alcohol such complete determinations were not possible, for the commercial mixture is too complex to allow account to be taken of the variations of density due to contraction. Hence the results could only show whether the variations in density would indicate uniform vaporization or selective vaporization.

In working with gasoline, whose mixtures produce neither appreciable contraction nor expansion, the nature of the portion vaporized could be determined.

Let P = the weight lost by the bottle, C;
D = the specific gravity at 15° C, of the liquid run out;
p = the weight of the liquid not vaporized;
d = its specific gravity at 15° C;
$\frac{P}{D}$ = the volume run out at 15° C;
$\frac{p}{d}$ = the volume of the liquid collected, measured at the same temperature.

$\frac{P}{D} - \frac{p}{d} = V$, the volume of the liquid vaporized.

$\frac{P - p}{V}$ = the specific gravity of the part vaporized, assuming it to be condensed to the liquid state at the temperature of 15°C.

Results equally valuable can be drawn from experiments with alcohol carburated with benzene.

The author has shown * that if carburated alcohol is diluted with twice its volume of salt water, the liquid separates into two very distinct layers. The lower layer is a weak alcohol solution not containing any benzene, while the upper layer contains all the benzene with a very little alcohol in solution. If this operation is repeated twice all the alcohol is eliminated and a measurement of the volume of the upper layer gives within a quarter of one per cent the volume of the benzene added to the alcohol, whether added as a denaturant or for the purpose of enriching the mixture. But the volume of the former was known, of course, to begin with.

Further still, in a study of alcohol denatured by gasoline with the help of amyl alcohol, the author determined as above the total volume of the amyl alcohol plus the gasoline, and proved by measuring the density that all the amyl alcohol remained in the liquid not vaporized.

The experiments whose descriptions follow show very accurately what happens in starting up a good surface evaporation carbureter, and also give a very clear idea of the disadvantages of a poor carbureter of the same type. Since it took from 13 to 15 seconds for the air to pass through the coil, during which time it was in close contact

* Note to the French Minister of Agriculture upon the methods of analysis of the carburated alcohols used at the competition of November, 1901.

with the liquid, it seems certain that the saturation was complete, especially at the high temperatures. In every case the results given below seem consistent.

French denatured alcohol (*Specific gravity* = 0.835 *at* 15° C.) — At a temperature of 11° C. the density of the liquid was not changed. One kilogram of the fuel required 46.381 cubic meters of air for its vaporization. Hence, it is impossible at this temperature to form a gaseous mixture suitable for good combustion.

At a temperature of 23° C. in the coil, the residual liquid collected in the flask, *D*, had a specific gravity of 0.835 at 14.5° C. Hence it was not appreciably altered. One kilogram required 5.970 cubic meters of air for its vaporization. Hence there is a satisfactory agreement between the results deduced theoretically from the vapor pressures and the results actually measured.

At a temperature maintained between 29.2° and 30° C., the specific gravity of the liquid collected was still 0.835 at 15° C. One kilogram required 4.147 cubic meters of air for its vaporization. The gaseous mixture is too rich.

At a temperature of 40° C, 17.6 per cent of the liquid introduced was vaporized. The specific gravity of the residual liquid was 0.836 at 15° C. Hence there was only a very slight selective vaporization. One kilogram required 1.958 cubic meters of air for its vaporization. Hence the mixture is very much too rich. It would be expedient to diminish the time of contact or to correct the mixture by the addition of pure air with vigorous stirring.

At 50° C, 27.5 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.836 at 15.7° C. There was still scarcely any change. One kilogram required only 1.316 cubic meters of air for its vaporization.

At 60° C., 56.9 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.836 at 15° C. One kilogram required only 0.713 cubic meters of air for its vaporization.

Thus, through a wide range of temperature, French denatured alcohol in the presence of an excess of air was vaporized without appreciable change of composition. But the temperature of the carbureter is very important, since the quantity of air necessary for the total vaporization of a given weight diminishes very rapidly as the temperature rises. This is a disadvantage in stationary or portable engines, since it is desirable to avoid requiring the constant presence of an attendant.

Dilute denatured alcohol. — In numerous reports on the industrial uses of alcohol in Germany it is stated that in that country 80 per cent alcohol by volume is used. This is a gross misconception. Instead, it is 80 per cent alcohol by weight, which is very approximately 85.6 per cent alcohol by volume.

In a series of experiments on alcohol of this type, it was found that at a temperature of 35° C., French denatured alcohol diluted to 85.5 per cent by volume, was materially changed. The specific gravity of the residual liquid was decreased in consequence of a selective vaporization of the methyl alcohol.

At 50° C. and upwards, there is proportional evaporation of the methyl and of the ethyl alcohol and the density increases.

The same alcohol was still further diluted until its specific gravity was 0.942 at 15° C. Tested as above at a temperature of 35° C, the residual liquid was perfectly clear and its specific gravity was 0.950. Hence the heavy benzene used as a denaturant had largely vaporized, and the alcohols equally had distilled. One kilogram

required 5.152 cubic meters of air for its vaporization. The gaseous mixture was too rich and the liquid much changed in its composition.

It is useful to note these variations, for in practice one does not have dry air such as was here used in order to make a progressive and scientific study of the question. In humid air if the evaporation is not complete and instantaneous, the alcohol not vaporized retains some water. Its strength is thus lowered, and in proportion as it is lowered there is a fractional vaporization which carries off the heavy benzene and the ethyl and methyl alcohols, leaving behind the water.

As has been seen, the denaturant exercises a beneficial influence by raising the vapor pressure of the mixture. Hence it is evident that the disappearance of the denaturant and the holding of the water hinder a constant and regular vaporization.

A rise of temperature of spray carbureters acts simultaneously on their discharge, on the quantity of liquid that can be vaporized in a given weight of air, and on the fractional vaporization of the different constituents. It is apparent, then, what practical difficulties and increased expense of operation are caused by spray carbureters and those dependent upon surface evaporation.

Equal volumes of alcohol and pure benzene (*Specific gravity* = 0.857). — This mixture contained equal volumes of 90 per cent ethyl alcohol and pure benzene. One kilogram of the mixture amounted to 1.1667 liters, or 0.5833 liter of benzene weighing 0.5133 kilogram and 0.5833 liter of 90 per cent alcohol weighing 0.4867 kilogram. The 0.5833 liter of alcohol consisted of 0.401 kilogram of pure alcohol and 0.085 kilogram of water.

At a temperature of 10.7° C., 12 per cent of the liquid was vaporized. The specific gravity of the residual liquid was

0.855. Hence it was weaker in benzene. As a matter of fact it contained only 44 per cent by volume of benzene. By a simple calculation from the densities it was found that there had evaporated 24.64 grams of benzene, 1 gram of anhydrous alcohol, and traces of water. Therefore, in 100 parts of vapor, benzene represented 96.1 per cent. Although the vapor pressure of benzene is but little higher than that of alcohol at first it is vaporized almost solely. One kilogram requires 3.291 cubic meters of air for its vaporization. The mixture is hence too rich.

At 19.6° C, 14.65 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.854 at 15° C. It contained 44 per cent of benzene in volume and the specific gravity of the aqueous alcohol remaining was 0.833 at 15° C. In the portion vaporized the ratio by weight of the benzene to the alcohol is reduced to $\frac{53.884}{9.116} =$ 5.910. In 100 parts of vapor, benzene represented 85.53 per cent. One kilogram of the mixture required only 2.176 cubic meters of air for its vaporization. Hence the mixture is much too rich.

At 29.75° C, 23.41 per cent of the mixture was vaporized. The specific gravity of the residual liquid was 0.854 at 15° C, and contained only 40.5 per cent of benzene by volume. The specific gravity of the alcohol left behind was 0.836 at 15° C. Hence there had been a selective evaporation of the alcohol leaving a more aqueous residue. The benzene represented 82.16 per cent of the portion vaporized. One kilogram required only 1.433 cubic meters of air for its vaporization.

At 39.7° C., 33.73 per cent of the mixture was vaporized. The residual liquid had a specific gravity of 0.852 at 15° C. and contained only 38.5 per cent of benzene by volume. The specific gravity of the residual alcohol was 0.8344 at

15°C. Hence at this temperature 90 per cent alcohol in the presence of benzene vaporizes almost without change of density. In 100 volumes of the liquid vaporized the benzene represents 68.97 per cent. One kilogram of this mixture requires 0.831 cubic meter of air for its vaporization.

At 50° C., 70.48 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.863. It contained only 23 per cent of benzene by volume. Hence a selective vaporization of benzene and alcohol had taken place leaving an aqueous residue. In 100 parts of the liquid vaporized the benzene represented 62.92 per cent. One kilogram required 0.491 cubic meters of air for its vaporization.

Hence selective vaporization is very evident in this complex mixture when it is brought in contact with an excess of air.

An alcohol mixture containing 25 *per cent of pure benzene by volume* (*Specific gravity* = 0.845). — At 12.5° C., 12.17 per cent of the liquid was vaporized. The residual liquid had a specific gravity of 0.845 at 15° C. and contained only 16.5 per cent of benzene by volume. Consequently the specific gravity of the alcohol remaining in the residue was 0.838 at 15° C. Selective vaporization of benzene and alcohol had taken place. One kilogram required 3.852 cubic meters of air for its vaporization. In the liquid vaporized, the benzene represented 90 per cent of the volume.

At 30° C., 21.85 per cent of the liquid was vaporized. The residual liquid had a specific gravity of 0.843 and contained only 12 per cent of benzene by volume. The specific gravity of the alcohol remaining in the residue was 0.8379 at 15° C. There was still selective vaporization of the benzene and alcohol leaving an aqueous residue. In

the liquid vaporized, the benzene was 62.19 per cent by volume. One kilogram of the liquid required 1.827 cubic meters of air for its vaporization.

At 50° C., 47.78 per cent of the liquid was vaporized. The residual liquid had a specific gravity of 0.843 at 15° C., and contained only 6 per cent of benzene by volume. The specific gravity of the alcohol remaining was 0.8415 at 15° C. Hence it was weakened. The benzene in the liquid vaporized represented 25.39 per cent by volume. One kilogram of the mixture required 0.783 cubic meters of air for its vaporization.

An alcohol mixture containing 12.5 *per cent of pure benzene by volume* (*Specific gravity* = 0.8354). — At 11° C., 10.42 per cent of the mixture was vaporized. The residual liquid had a specific gravity of 0.841 at 15° C., and contained only 4 per cent of benzene by volume. The residual alcohol had a specific gravity of 0.8383 at 15° C. Hence there had been selective vaporization of the benzene and alcohol. In 100 parts of the liquid vaporized, benzene represented 88.28 by volume. One kilogram of this mixture required 6.269 cubic meters of air for its vaporization.

At 30.5° C., 16.95 per cent of the liquid was vaporized. The residual liquid had a specific gravity of 0.840 at 15° C., and contained only 2.5 per cent of benzene by volume. The alcohol remaining had a specific gravity of 0.8739 at 15° C. Hence there had still been selective vaporization of the benzene, and especially of the alcohol, leaving the aqueous residue. In 100 parts of the liquid vaporized, benzene represents 83.52 per cent. One kilogram of the mixture required 2.698 cubic meters of air for its vaporization.

At 49.5° C., 41.46 per cent of the liquid was vaporized. The residual liquid had a specific gravity of 0.840 at 15° C.,

and contained only 1.5 per cent of benzene by volume. The residual alcohol had a specific gravity of 0.8373 at 15° C. Hence, at this temperature, it appears that the mixture of alcohol and benzene carries away more water in its vaporization than at lower temperatures. One kilogram of the mixture requires 1.089 cubic meters of air for its vaporization.

Finally, if it is assumed that the passage through the coil was so rapid as not to alter too extensively the initial composition of the mixture, it may be concluded that spraying with subsequent incomplete vaporization is not favorable for regular carbureting. At first, there would turn into vapor a mixture very rich in benzene (up to 90 per cent,) and containing alcohol a little more concentrated than in the original mixture. The mixture of air and liquid would be much too rich for any rise of temperature however slight. Hence it would be necessary to have recourse to a supplementary introduction of fresh air, which must vary, moreover, with the temperature. This is contrary to the economic principle of simplicity in operation which has been stated for stationary and portable engines.

If the temperature of the carbureter rises and if the spray orifice introduces accordingly more than the quantity regulated at the time of starting, the ratio of the benzene vaporized to the alcohol will be always high but always diminishing. Below a certain temperature the residual alcohol will be more aqueous than the alcohol introduced, and accordingly less volatile. Hence it would finally reach a stage where it would only be taken along in the state of small drops.

It is near the normal temperature that the vaporized mixture is richest in benzene; accordingly, if there is not from the start total vaporization, the carbureter will con-

tain on its solid surfaces a liquid from which the benzene will disappear rapidly, and the mixture presented to the air will become less and less volatile.

Around a certain temperature between 40° and 50° C., the 91 per cent alcohol is uniformly vaporized; above that temperature it distils and leaves a more aqueous residue which is only able to be carried forward mechanically.

Conversely, if it is supposed that a homogeneous mixture of air and the vapors considered be introduced into a cold explosion chamber, there will remain in the form of vapor only a mixture rich in benzene; the remainder will condense on the walls during the first stroke and will not possibly be able to be distributed uniformly throughout the whole mass during the compression stroke. Thus there will be incomplete combustion and poor utilization of the fuel, perhaps even the formation of aldehydes and acids and carbon.

The petroleum hydrocarbons. — In accordance with the method previously followed the French commercial gasolines used in engines will be compared with carborated alcohol and French denatured alcohol. The gasolines used were those whose composition is shown on pages 130 to 132.

Benzomoteur (*Specific gravity* = 0.7125 *at* 15° C.). — At 14.8° C., 21.86 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.721. Calculating as before the specific gravity of the portion vaporized, it was found to be 0.683. Hence the most volatile portions predominated there in a remarkable manner, and there was as before selective vaporization. One kilogram of the portion vaporized required only 2.572 cubic meters of air for its vaporization. The mixture was, then, too rich.

At 21° C., 19.13 per cent of the liquid was vaporized.

The specific gravity of the residual liquid was 0.721 at 15° C. Consequently the portion vaporized was almost the same in composition as in the preceding experiment. One kilogram required only 1.983 cubic meters of air for its vaporization.

In addition, the residual liquid was distilled in a Schloesing ammonia still until the vapor reached a temperature of 77° C. The quantities at different temperatures were as follows:

Temperature. Degrees Centigrade.	Quantity Collected. Per Cent.	Specific Gravity.
15 to 44	2.63	0.669
44 to 52	3.42	
52 to 52	4.47	
52 to 55	4.10	
55 to 62	2.63	0.709
62 to 77	6.84	
	24.09	

There was a decided fractional vaporization of the lighter portions.

At 30° C., 23.98 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.722 at 15° C. Consequently the specific gravity of the portion vaporized was 0.683 at 15° C. There was, then, still a predominance of the most volatile portions in the part vaporized. One kilogram required only 1.497 cubic meters of air for its vaporization.

At 40° C., 48.03 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.7265 at 15° C. Consequently the specific gravity of the portion vaporized was 0.698. Hence there was a carrying over of the heavier portions. One kilogram required only 1.385 cubic meters of air for its vaporization.

At 50° C., 56.62 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.7255 at 15° C. Consequently the specific gravity of the liquid vaporized was 0.703. One kilogram required 1.064 cubic meters of air for its vaporization. According to these results, it would be necessary for the temperature to rise to at least 60° C., in order to vaporize uniformly the *benzomoteur* tested.

Stelline (*Specific gravity* = 0.700 *at* 15° C.). — At 11° C., 17.60 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.7053. Hence the specific gravity of the portion vaporized was 0.6755. One kilogram of the portion vaporized required 2.152 cubic meters of air for its vaporization.

At 21.3° C., 26.73 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.710 at 15° C. Hence the specific gravity of the portion vaporized was still 0.6755. Hence there had still been selective vaporization of the lighter portions. One kilogram of the liquid required 1.619 cubic meters of air for its vaporization.

At 31° C., 32.20 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.712 at 15° C. The specific gravity of the portion vaporized was 0.676. Hence the portions evaporated between the temperatures of 11° and 31° C. have very nearly the same composition. They are the lighter hydrocarbons. One kilogram of these required only 1.233 cubic meters of air at 31° C. for their vaporization.

At 40° C., 50.0 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.7115 at 15° C. The specific gravity of the portion vaporized was 0.685 at 15°. Hence heavier portions of the liquid were carried over. One kilogram of the portion vaporized required only 0.861 cubic meter of air for its vaporization.

At 50° C., 58.19 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.714 at 15° C. Hence the specific gravity of the portion vaporized was 0.690 at 15° C. One kilogram of it required only 0.604 cubic meter of air for its vaporization.

According to these results apparently *stelline* would be entirely vaporized between 60° and 70° C.

The following table gives the per cents of the residues, from the various experiments, which boiled away below 72° C.

	Per cent boiled away from —	
	35° to 60° C.	60° to 70° C.
After passage of air at 11° C	10.28 (1.)	21.98 (2.)
After passage of air at 21°	6.46	10.93
After passage of air at 31°	6.31	7.32
After passage of air at 50°	5.82	4.58

(1.) Specific gravity = 0.647. (2.) Specific gravity = 0.667 to 0.682.

Mixture of the portions of Stelline and Automobiline boiling off between 12° *and* 77° C. (*Specific gravity* = 0.666 *at* 15° C). — At 12° C., 51.05 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.676. Hence the specific gravity of the portion vaporized was 0.657. Hence there was selective vaporization even in a liquid so volatile as this. One kilogram required 1.194 cubic meters of air for its vaporization.

Mixture of the portions of Stelline and Automobiline boiling off between 70° and 137° C. (*Specific gravity* = 0.727 *at* 15° C). — At 10.85° C., 9.58 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.728 at 15° C. Hence the specific gravity of the portion vaporized was 0.717. One kilogram required 4.470 cubic meters of air for its vaporization.

At 20.75° C., 11.87 per cent of the liquid was vaporized.

The specific gravity of the residual liquid was 0.7287 at 15° C. Hence the specific gravity of the portion vaporized

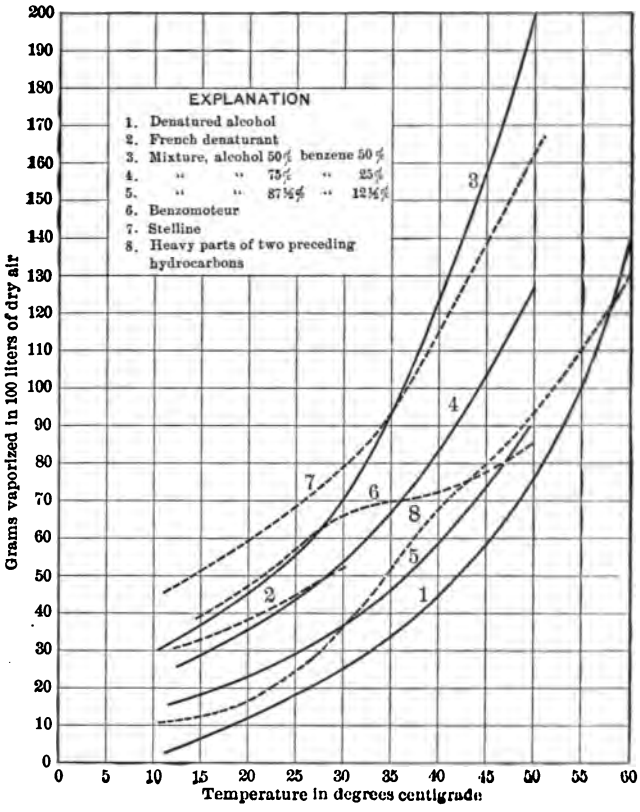


FIG. 22.

was 0.717. One kilogram required 3.900 cubic meters of air for its vaporization.

At 30° C., 20.10 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.729 at 15° C. Hence the specific gravity of the portion vaporized was 0.718. One kilogram required 2.131 cubic meters of air for its vaporization.

At 40° C., 28.35 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.7305 at 15° C. Hence the specific gravity of the portion vaporized was 0.718. One kilogram required 1.453 cubic meters of air for its vaporization.

At 50° C., 36.66 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.732 at 15° C. Hence the specific gravity of the portion vaporized was still 0.718. One kilogram required 1.083 cubic meters of air for its vaporization.

At 70° C., 68.96 per cent of the liquid was vaporized. The specific gravity of the residual liquid was 0.736 at 15° C. Hence the specific gravity of the portion vaporized was 0.723. One kilogram of it required 0.670 cubic meters of air for its vaporization.

Fig. 22 shows graphically the results of these experiments.

Disadvantages of carbureters acting by surface evaporation. — The previous experiments make clear the disadvantages of those carbureters in which the air circulates in a thin layer over a liquid surface kept at constant level by a float permitting a gradual entrance of the fuel mixture, also those in which the air flows under a barrier across the surface of a supply of the liquid supposed to be sufficient and introduced once for all. In both cases the mixture may be heated by a portion of the exhaust. Nothing is less safe than this type of carbureter. On the one hand, the quantity of air drawn in at each suction of the cylinder varies with the vapor pressure of the liquid in the carbureter at that instant; on the other hand, the quantity of air necessary to evaporate a kilogram of the fuel varies with the temperature of the liquid and its composition. Hence the opening for the supplementary admission of air must continually be changed by trial, an

obvious inconvenience. It may happen that the mixture after a time will become too weak, although at first it was too rich, and that the contents of the carbureter must be thrown away. This necessity should not be attributed to the humidity of the air condensed, for an intimate mixture of water and a substance insoluble in water such as a hydrocarbon has a vapor pressure higher than the hydrocarbon has, the latter maintaining its own proper pressure. The moisture present is only able to affect the quantity of air drawn in and the temperature of combustion. The explanation often offered is only applicable to mixtures of water and soluble substances such as the alcohols.

It has been seen that if the temperature is sufficiently low (from 10° to 30° C., for example), the portion of the liquid vaporized varies only slightly in composition, but it is chiefly formed of the more volatile portions of the liquid mixture.

The phenomenon is much more complex when one considers fractional distillation. It may even happen that some of the higher homologues in the series are removed the most rapidly.

Suppose, for example, two substances which do not react on each other, calling p and P the weights of the two substances vaporized at a given temperature, d and D their vapor densities, and t and T their vapor pressures at that temperature. Then

$$\frac{p}{P} = \frac{d}{D} \times \frac{t}{T}.$$

If, as in the cases under consideration, the vapors are greatly expanded, their densities are proportioned to their molecular weights, m and M, and then

$$\frac{p}{P} = \frac{m \times t}{M \times T}.$$

But in a series of homologous substances, like the principal components of gasoline, m and t vary in the opposite direction, t decreasing as m increases. Hence there is established a sort of compensation as soon as the temperature is high enough, so that above a suitable temperature the composition of the mixed vapors approaches more and more that of the liquid mixture.

In the case of mixtures of alcohol and benzene, doubtless because these bodies are not soluble in each other in all proportions, the influence of temperature is different. The mixed liquid has a vapor pressure appreciably higher than that of the two constituents and its value varies slightly with the relative proportions. Hence the previous reasoning is not applicable. Still in this case temperature has an effect. It has been seen that the relative proportion of 90 per cent alcohol vaporized by a current of air increases as the temperature rises.

Temperature in spray carbureters. — In spray carbureters a limited quantity of the fuel is projected into a current of air and is more or less divided, for example, on metallic gauze, which is traversed by a current of air already more or less saturated with the most volatile vapors and also more or less cooled by their volatilization. This air, coming in contact with the less volatile liquid, absorbs a certain quantity of it, providing the temperature permits.

But as has been seen in studying the flow through capillary tubes, the amount sprayed varies rapidly with the temperature possessed originally by the liquid or which is communicated to it by the metal in contact with it. On the other hand, the more of the fuel vaporized in a given weight of air, the less will be the suction exerted by the carbureter, and the less the discharge of liquid. Hence the temperature acts in two opposing ways but with

the results not compensating very exactly. One moves in a tangled web when he deals with stationary or portable engines, where the use of an attendant is to be avoided so far as possible.

If the temperature of the air and of the liquid is low, there will be vaporization of only the most volatile constituents. The example of alcohol and benzene is very plain on this point. The remainder of the mixture is retained on the metal gauze which partially throttles the passage. In consequence, the vacuum is increased and if the gauze is fine, the foggy liquid is drawn along mechanically by the high velocity of the air.

The mixture is thus very heterogeneous, more especially as the air is generally overcharged and it is necessary to resort to the introduction of pure air beyond the throttle. Thus the spray is diminished in an unknown and variable proportion according to the temperature, whence a series of trials are necessary.

Carbureting by bubbling. — In certain types of carbureters, rare, it is true, contact of air and fuel is secured by bubbling the air under a pressure of 15 to 20 millimeters through the liquid kept at constant level.

The liquid in the carbureter gives up to the air the more volatile portions, which are immediately replaced by an equal volume of the original mixture. Vaporization of the more volatile constituents will not be complete as they will be more or less retained by the less volatile constituents. The latter will be partially vaporized with the former, as found on page 184 and explained on page 192.

Yet it can be proved quickly that the composition of the liquid remaining in the carbureter will become less and less suitable for a constant and satisfactory vaporization.

After the long experiments summed up above, relative

to the study of surface carbureters in which, in spite of the velocity of circulation, the liquid undergoes an appreciable change in composition, as soon as the temperature reaches certain values, it seemed unnecessary to repeat similar tests on all the various mixtures previously studied and further experiments were limited to certain especially interesting mixtures.

In order to study the question properly the ordinary carbureter operating by bubbling was not employed. These are generally small. The dimensions were increased in order to have a sufficient quantity of the liquid to permit a careful examination. Moreover, by increasing the length of time of the operation, the same final state was obtained as with smaller apparatus. Hence it should be remembered that in practice the results would happen much quicker than shown by the results of these tests.

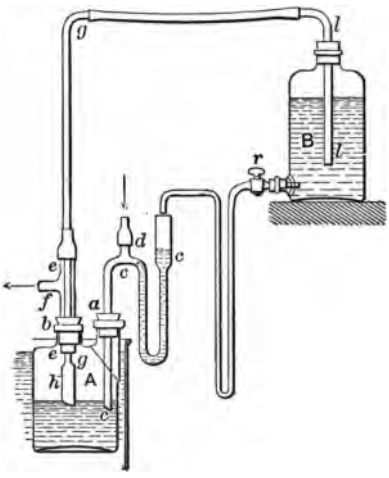


FIG. 23. CARBURETING BY BUBBLING.

Fig. 23 shows the apparatus used. The carbureter proper is formed by a two necked bottle, *A*, immersed in a bath kept at a constant temperature. In the neck, *a*, is fixed by means of a cork an *s*-tube, *c-c*, provided with a branch for the entrance of dry air measured by an accurate meter. The volume recorded by the meter was reduced to normal pressure as explained on page 175. The end of the tube, *c-c*, was cut on a slant and dipped 16 millimeters below

the surface of the liquid in the bottle, *A*. The other end of the tube, *c-c*, was expanded into a funnel fed by a Mariotte bottle, *B*, which will be discussed later.

The second neck, *b*, of bottle *A* was connected to a large tube, *e* – *e*, furnished with a branch, *f*, through which the mixture of air and vapor flowed out. In the axis of tube *e* – *e* there was fixed by a rubber cork a narrow tube, *g* – *g*, terminated at its lower end by an enlargement, *h*. This was cut at an angle and just reached the level of the liquid in the bottle. The tube *g* – *g* communicates directly with the tube *l* – *l* of the Mariotte bottle *B*. When this is arranged and the cock, *r*, is opened, no air can enter *B* except when the extremity of *h* is uncovered.

In this way an almost absolutely constant level in the bottle, *A*, is maintained.

To perform an experiment, the bath is raised to the desired temperature and kept there constantly by a good thermo-regulator. The bottle, *A*, was weighed perfectly dry, then filled with the liquid to be used up to the desired level. The *s*-tube was connected and its exterior branch was filled up to the level, *d*. The weight of the liquid added was obtained by the increase in weight. The Mariotte bottle, *B*, was regulated to give a very slow flow and weighed. Then everything was put in place and the tubes *g* and *l* were joined.

The time and the reading of the meter were noted and the experiment was started by adjusting the entrance of air through the tube, *d*, and opening the stopcock, *r*. Soon the Mariotte bottle, *B*, commenced to work regularly. At the end of a suitable time, generally about three hours, the experiment was stopped. Again the time and the meter reading were noted, the flow of air was stopped by disconnecting the tube, *d*, from the drying tubes, and the flow of

liquid was shut off by closing the stopcock, *r*. The bottle, *A*, was weighed, and the loss of weight in the Mariotte bottle, *B*, was determined.

The results of the most striking experiments were calculated as follows:

Mixture of equal volumes of 90 *per cent alcohol and pure benzene.* — The experiment lasted 3 hours, 8 minutes, at a temperature of 22° C. The empty bottle, *A*, with its accessories weighed 280 grams. Filled it weighed 370 grams. Consequently it contained 90 grams of the alcohol mixture. The Mariotte bottle at the start weighed 2628 grams. At the end of the experiment the bottle, *A*, weighed 361 grams and hence contained 81 grams of the liquid. The Mariotte bottle weighed 2587 grams.

There had been exposed to the action of evaporation, $90 + 2628 - 2587 = 131$ grams.

The specific gravity of the initial mixture being 0.857 at 15° C., the volume of the 131 grams at 15° was 153 cubic centimeters, of which $153 \div 2 = 76.5$ cubic centimeters, corresponding to 67.63 grams, represents the benzene used.

The specific gravity of the residue contained in the bottle, *A*, was 0.848 at 15° C. According to analysis the residue contained 29.75 per cent by volume of benzene. Hence the volume of the residue was 95.75 cubic centimeters containing 28.5 cubic centimeters of benzene, weighing 25.19 grams.

Hence the portion vaporized, $131 - 81 = 50$ grams, would have occupied at 15° C. $153.00 - 95.74 = 57.26$ cubic centimeters, and would have contained $76.5 - 28.5 = 48$ cubic centimeters of benzene, or 42.43 grams, which was 84.86 per cent of the entire weight of the portion vaporized. The specific gravity of this portion would have been 0.873 at 15° C.

The alcohol vaporized was

$$57.26 - 48.00 = 9.26 \text{ cubic centimeters}$$

and weighed $50.00 - 42.43 = 7.57$ grams.

It would have had a specific gravity of 0.8105 at 15° C., corresponding to a strength of 96.2 per cent. In this calculation no account is taken of the contraction of the alcohol water mixture which is negligible between 90 and 96 per cent.

Hence there was selective vaporization, especially of the benzene as previously observed, and slightly of concentrated alcohol. The residue contained 55.81 grams of alcohol diluted to 66.24 cubic centimeters, giving a specific gravity of 0.842 at 15° C., or a strength of 87 per cent.

During the experiment 156 liters of dry air passed or 49.82 liters per hour. One hundred liters vaporized 29.55 grams, or one kilogram of the portion vaporized required 3.627 cubic meters of air for its vaporization.

Referring to the trickling experiment where the liquid was constantly renewed in a thin layer, it was found that at 20° C., 100 liters of dry air vaporized 45.95 grams. The proportion of benzene was practically the same, 85.5 per cent by weight, but the residue contained 44 per cent of benzene. The density of the residual alcohol was 0.8336.

It is probable then that at the beginning of the bubbling the vaporized portion of the mixture contained more than 85 per cent by weight of benzene. As the vaporization weakened, the mixture there was vaporized but little more benzene than that furnished by the new liquid introduced, since the strength of the vapor in benzene was not appreciably diminished.

The same experiment was repeated at a temperature of 40.25° C. for 3 hours, 34 minutes. The liquid vaporized

contained 78.75 per cent of benzene by volume or 79.73 per cent by weight.

The portion vaporized still had a specific gravity of 0.873 at 15° C. The alcohol vaporized had a specific gravity of 0.8328, or a strength of 89.8 per cent.

Hence there was still selective vaporization of the benzene, but the alcohol was scarcely modified. As for the residual liquid alcohol, its specific gravity was 0.8363 by calculation. Thus as regards the alcohol, the residue is less modified as the temperature of the carbureter is raised.

Hence, when the partially evaporated liquid is not removed from the carbureter, a relatively high temperature may be reached, but it is necessary to exceed slightly 160° C., the boiling point of the mixture of equal parts of alcohol and benzene, in order not to have a residue weaker than the initial mixture.

In the last experiment 100 liters of dry air vaporized 59.89 grams of the portion evaporated or 1 kilogram of the mixture required 1.669 cubic meters of dry air for its vaporization.

Stelline. — For comparison, stelline, previously used, was studied in the bubbling apparatus. The first experiment was made at a temperature of 20° C. It lasted 3 hours, 20 minutes, with a discharge of 55.20 liters of dry air per hour.

The specific gravity of the portion vaporized was 0.682 at 15° C., distinctly less than that of the initial mixture. Hence there was selective vaporization. One hundred liters of air vaporized 35.87 grams, or 1 kilo of the light constituents vaporized required 2.787 cubic meters of dry air for its vaporization.

At the end of the experiment the liquid remaining in the bubbling apparatus had a specific gravity of 0.716

at 15° C., while the specific gravity of the initial liquid was 0.700.

In a second experiment, at a temperature of 40.3° C., lasting for 3 hours, 7 minutes, with the air flowing at the rate of 64.70 liters per hour, the specific gravity of the residue was 0.720 at 15° C., and the specific gravity of the portion evaporated was 0.677. Thus, the lighter constituents predominated in the portion vaporized more than in the previous case, which is just opposite from the results obtained with the alcohol benzene mixture.

One hundred liters of air vaporized 61.54 grams of the more volatile constituents, or 1 kilogram required 1.626 cubic meters of dry air for its vaporization.

Resumé. — It has been shown that the simple and relatively light apparatus employed in automobiles where the constant presence of a chauffeur is necessary, is not suited in practice to the requirements of economical stationary or portable engines.

It is necessary, therefore, to direct the efforts of manufacturers toward the study of carbureters, by showing them the irregularities arising from the use of apparatus based upon spraying, surface evaporation, or bubbling, whenever the temperature of the carbureter is exposed to appreciable variation during the time of operation.

Moreover, already certain engines are built suitable for kerosene. These have operated very well when tried on alcohol either denatured or carburated. Nevertheless, it will be well to apply to certain of them some modifications in detail such as the extension of the heated surface and the enlargement of the admission valves.

Moreover, there may be tolerated a poor combustion during the first few strokes while the carbureter is not sufficiently warm, nor the engine sufficiently loaded.

This slight inconvenience of alcohol either denatured or

carburated may be largely avoided by starting the engine with a small quantity of gasoline or benzene. Since some automobile engines operate in this way, it is certainly practicable for stationary engines where weight and complications are not so objectionable.

CHAPTER IX.

EFFECT OF TEMPERATURES BELOW THE TEMPERATURE OF COMBUSTION.

Introduction. — All that precedes this chapter, except what relates to determining the amount of air theoretically necessary for combustion, belongs properly to physics.

It has been shown that the minimum temperature of the various combustible mixtures should be, after the complete vaporization of the liquid used, to prevent condensation, and the formation of heterogeneous mixtures incapable of complete combustion.

The author has discussed at some length the difficulties, due to variation of temperature, that most of the carbureters in use present, from the point of view of regularity of the carbureting while the engine is running.

Up to the present time the question has been very little studied by manufacturers. It is, however, important when explosion engines are used for industrial purposes.

The question is as important from a chemical point of view as from a physical. Therefore the chemical side of the question will now be presented.

This study appears the more necessary because the minimum temperature of change of molecular structure of alcohol as given in the standard text-books is much too high, and there has been too little investigation of the changes that may take place even when there is no evident decomposition of the molecules. The author has observed that very important changes may be produced, either in the carbureter close to the admission valve, or in

Number.	Admission Valve.	Exhaust Valve.	Liquids Condensed from Products of Combustion and Remarks.
2	Fairly clean on the outside	Fairly clean on the outside, seat very clean	Liquid, yellowish, slightly acid.
3	The same	The same	Liquid, slightly acid, soot.
4	The same	Fairly clean	Liquid, variable, yellow, slightly acid.
6	Soot on the outside	Clean	Condensation slightly acid, traces of acetaldehyde; exhaust at the temperature of melting silver.
7	Tar on the outside	Lampblack and corrosion	Liquid, slightly acid.
9	Fouled	Fouled	Liquid, yellowish, slightly acid.
11	Fairly clean	Fairly clean	Liquid, very acid.
12	Nothing on the outside	Clean	Liquid, slightly acid, containing soot.
14	Gummed up with tar	Corroded	Liquid, acid, acetic, acid vapor.
15	Dry, fairly clean	Dry, fairly clean	Much sooty smoke; liquid very decidedly acid.
18	Very clean and dry on the outside; slightly corroded on the inside	Slightly corroded	No odor nor smoke; liquid very slightly acid.
19	Very clean	Very clean	Liquid, yellow, very acid.
20	Clean	Clean	Liquid, slightly acid, with a little smoke from time to time.
21	Very clean	Very clean	Liquid, slightly cloudy, traces of soot, traces of aldehyde, slight smoke.
22	Fairly clean	Fairly clean	Liquid, acid.
23	Very clean	Corroded	Very abundant condensation, smelling of alcohol, acid.
25	Very clean	Very clean	Liquid, clearly acid.
26	Dry and clean	Very clean	Liquid, very decidedly acid, slightly doubtful, a little soot.
27	A dry, black coating on the outside	Fairly clean	Odor of garlic at the start, abundant smoke which gradually diminishes, liquid decidedly acid.
28	Very clean	Very clean	Smoke very abundant during the whole run; benzene in the burned gases which came from the denatured alcohol not carburated.
31	Very clean	Very clean	Liquid, slightly acid.

troubles that arise from them, are attributable not merely to the chemical nature of the alcohol, but also to the manner of using it for the production of the explosive mixture, and perhaps even to the method of denaturing it.

In many engines the two valves are placed one above the other in the same small chamber. Thus their inspection is made easy. Some engine makers, who adopt this manner of placing the valves, do so with the intention of cooling the exhaust valve by the flow of the cool gases coming from the carbureter, since they think the water jacket around the seat of the exhaust valve is not sufficient protection against the action of the highly heated burned gases. On the other hand, however, the admission valve becomes heated by contact with the burned gases which touch it during the period of exhaust.

In other engines the two valves have their axes parallel, and are placed in two chambers lengthening out the cylinder and passing through the water jacket. It is evident that the admission valve is then heated for a shorter time, and consequently reaches a less high temperature.

Either one of these arrangements seems to give but little trouble when gasoline is used for fuel. At the most, sometimes traces of lampblack are found on the side of the admission valve, a little corrosion on the interior of the exhaust valve, at times a slight deposit of tar and coke upon the part of the exhaust valve facing the engine cylinder when the flow of lubricating oil has been too great. The trouble from corrosion disappears when nickel valves are used.

The results given above show that *this is not always the case* with alcohol. It is the opinion of the author that marked difficulties with alcohol appear if the carbureter has not completely and instantly vaporized the fuel in a homogeneous manner, before it comes in contact with the

hot metal of the admission valve, or before it is highly heated during the compression stroke from contact with gases remaining from the preceding explosion.

In each case, abrupt vaporization of the little drops of the liquid will take place, which causes the formation of a layer of vapor between the valve and the air contained in either the carbureter or the cylinder. Then a more or less complete diffusion of these vapors takes place, from which results a mixture which grows richer in oxygen as zones more remote from the heated valve are considered.

Further, in the above two cases, when the admission valve opens some too rich vapor mixture will be poured into the neutral gases contained in the combustion chamber, then the air in excess mingled with the really vaporized part of the next charge of fuel. In spite of the violent agitation produced by the rapid return of the piston, and even because of the rapidity, it is improbable that a homogeneous mixture is produced, especially when the cylinder is cold.

There will then be incomplete combustion, as has been observed, and which may even be shown by the production of smoke. In any case, the fuel will be incompletely utilized and an increased expense per horsepower per hour will result.

But while the light petroleum hydrocarbons and even the heavier ones of the same series are less affected by heat, since they have been distilled, and are only modified to any extent by contact with the valve,* when oxygen is present, alcohol and its homologues and their derivatives whose molecules contain oxygen, may undergo very serious modifications at temperatures plainly inferior to that of the valves.

* In the case of either crude or refined petroleum, it is clear that decomposition may be caused by heat from contact with the piston and with the combustion chamber if the latter is not cooled.

In the first part of this work, the apparent equilibriums have been shown that may result in such simple mixtures as $H_2 + O$ and $CO + O$, according to the temperature, and dependent upon whether the phenomenon is adiabatic or isothermal. More complex reactions may be expected if the molecule is more complicated.

The author not having at hand the means to experiment with adiabatic reactions, tried to obtain the best possible results from isothermal reactions which seemed to him to have more bearing on the subject under consideration. To tabulate as much as possible the experiments and see their results, the subject to be studied will be divided as follows:

1. The action of relatively moderate temperatures upon the alcohols or their derivatives.

2. The rapid action of moderate temperatures in the presence of burned gases (anhydrous carbon dioxide) and small quantities of air.

3. The rapid action of the common metals alone, on the alcohols or their derivatives.

The first case has been divided into two parts.

1. A. The instantaneous action of heat upon a current of vapor.

1. B. The much slower action permitting a better determination of the successive products of reaction.

CHAPTER X.

INSTANTANEOUS ACTION OF TEMPERATURES RELATIVELY MODERATE UPON ALCOHOL VAPORS OR THEIR DERIVATIVES.

Method of operation. — This preliminary study has seemed necessary to eliminate as much as possible the effect of the duration of the experiment which, as has been seen in the first part of this study, may exert a very great influence, the effect of time being able to replace the effect of temperature. In many of the phenomena relating to explosion engines, the time of the initial reaction may vary greatly.

An attempt has been made to study the primary reactions, and separate them from the much more complex reactions which take place on the products of the first reaction. It was hoped that quite definite results would be obtained by this method.

To obtain isothermal conditions easily reproduced and to assure the rapidity of the reactions at a known temperature, the apparatus described below (Fig. 24) was used.

A continuous current of carbonic acid gas was obtained by the action of dilute hydrochloric acid on broken marble contained in a bottle with a bottom opening connected to an overflow large enough not to be obstructed by deposits of silica, the residue of the marble, and ending at a level high enough so that the liquid column overcame all the interior resistance of the apparatus, while allowing the marble to be completely submerged. The hydrochloric

acid diluted to one third was admitted drop by drop from a Mariotte flask into a large safety tube. The gas set free necessarily contained a trace of air introduced by the acid. The oxygen was absorbed continuously by bubbling the gas through a long glass pipe slightly inclined containing a clear suspension of ferrous hydrate. (Manganous hydrate would have produced the same result.) The

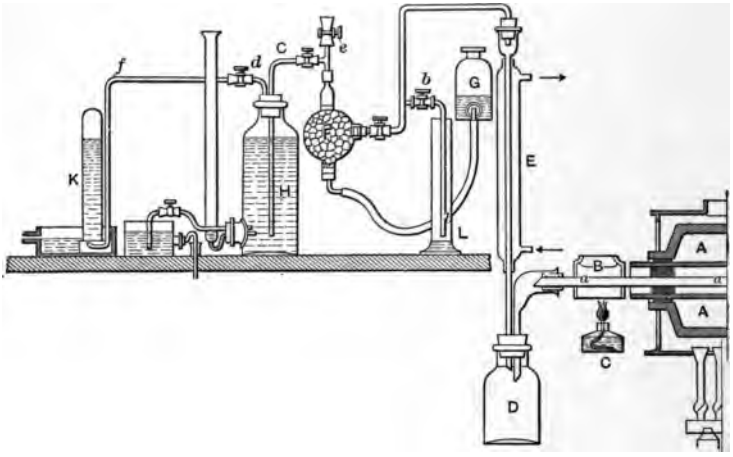


FIG. 24. EFFECT OF LOW TEMPERATURES ON ALCOHOL VAPORS.

traces of hydrochloric acid carried along were absorbed in a large tube containing fine chalk. Then the gas, consisting of carbon dioxide and a trace of nitrogen, to be used for carrying along the vapors to be studied, was dried in two large tubes containing fused calcium chloride.

A current of gas with a practically constant velocity was thus obtained.

This gaseous mixture was bubbled through a forked tube into a bottle containing at least half a liter of the liquid experimented on. Former experiments gave very approximately the composition of the vapors carried along.

The bottle was plunged into a bath furnished with a good Schloesing thermo-regulator. The mixture of gas and vapor was dried in a tin coil plunged in the same bath.

The gas on coming out from the coil entered a hot tube or Bohemian glass, *aa*, Fig. 24, having an interior diameter of 5 millimeters and a length of 600 millimeters, surrounded by an air bath inside a casting, *A*, weighing 30 kilograms, whose mass permitted the temperature to be easily regulated. This air bath formed by a horizontal cylinder with thick walls, and equipped with two horizontal openings and a vertical tube that held a thermometer, was warmed by a gas range that could be easily regulated and surrounded with sheet iron lined with asbestos. It was easy to keep the interior of the air bath within two degrees of the desired temperature.

To avoid any condensation, the extremities of the tube, *aa*, were surrounded with a small sheet iron casing provided with a chimney and slightly warmed by a small alcohol lamp, *C*.

The mixture of gas and vapor next entered the bottle, *D*, closed with a cork pierced by two holes. The second hole contained the lower end of the vertical cooling tube, *E*, which returned the condensible liquids into the bottle, *D*.

The uncondensed vapors next passed through a bent tube in a little mercury bath into a spherical flask, *F*, filled with glass beads and containing a solution of caustic potash, 40 Baumé. The spherical flask was connected at its lower end with a bottle, *G*, containing the same solution that could be renewed as required. The upper part of this spherical flask was drawn out into a fine tube that connected with a *T* tube, whose vertical branch, closed during the experiment, allowed the gases to escape at the beginning of the experiment, and through which at the end the

liquids collected by the potash could be drawn out. The horizontal branch was connected with a sort of Mariotte bottle, *H*, under a constant pressure, filled with a concentrated solution of calcium chloride which dissolved the traces of alcohol vapor brought over, without absorbing an appreciable amount of the gases obtained. Moreover, the analyses made were generally qualitative and a slight absorption could be neglected. In addition, at the beginning of each experiment the solution was saturated with the gaseous products. The carbonic acid gas was almost entirely absorbed in the flask of potash.

Any aldehyde produced which had escaped condensation in the cooling tube was polymerized rapidly in the same spherical flask, owing to the temperature developed by the formation of carbonate of potash. It could then be determined qualitatively, either in the liquid collected in the bottle, *D*, according to Gayon's reaction based upon the reaction of bisulphite of rosaniline, or in the potash through the yellow color that it communicated to this reagent.

There reached then the bottle, *H*, only a little nitrogen, some of the gases arising from the reaction, and traces of carbonic acid gas that escaped the action of the more or less saturated carbonate of potash. The nitrogen served to keep in a state of vapor some small amount of hydrocarbon products which would have been condensed except for the nitrogen at ordinary temperatures, and would have escaped detection. At the end of the experiment the gases collected in *H* were forced into the tube, *K*. They were then transferred under mercury into a test tube containing pieces of fused potash. Next all traces of oxygen that might have been introduced into the tube during the transferring were absorbed by the action of a very small amount of pyrogallic acid in the presence of the excess of potash.

Very often a study of the specific gravity of the liquid bodies resulting from the reaction was sufficient to determine the nature of the reaction.

However, in the case of alcohols, the variations of specific gravity would have given only approximate results.

Attentive observation of the phenomena enabled the author to overcome this difficulty. Nearly always a determination of the specific gravity was sufficient. But it sometimes happened that the condenser collected only very small quantities of liquid, from 3 to 10 cubic centimeters. Under such conditions it would have been unwise to use the specific gravity bottle.

The difficulty was avoided by the use of apparatus, represented in Figs. 25 and 26, based upon the theory of communicating tubes in which the heights of the two liquids in equilibrium are in inverse ratio to their specific gravities.

Fig. 25 shows a simple apparatus applicable to the case of liquids insoluble in water. It consists of two connecting tubes, 15 millimeters in interior diameter at their largest parts. One, *A*, intended to contain distilled water, is of a uniform caliber above the common zero mark and is divided into millimeters; the other is formed by a small tube, *B*, which at 250 millimeters above the zero mark enlarges into tube, *C*, having the same caliber as tube, *A*, and also divided into millimeters. A thermometer showing tenths of a degree is fixed between the two tubes. A glass stopcock, *D*, allows the water to be run out until the meniscus of separation of the two liquids stands at zero. In the present case the organic compound is lighter than water. It can then always be so arranged that the meniscus of separation is in branch, *B*. Under these conditions the reading of the upper level of the liquid to be studied can be made in tube, *C*, where the influence of capillarity

is small, provided there are about 4 cubic centimeters of liquid.

To perform the experiment a flask of distilled water and the flask containing the liquid to be studied are left for some time upon the base of the apparatus, so that the

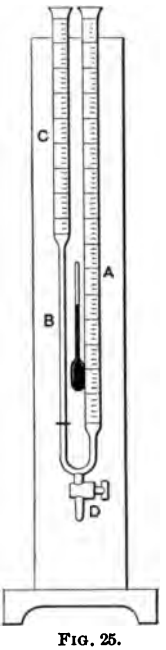


FIG. 25.

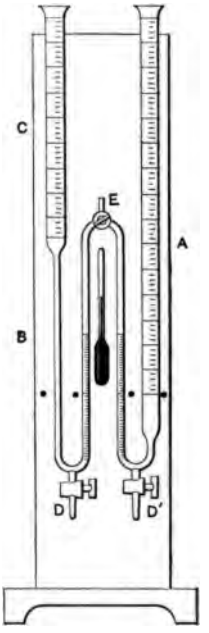


FIG. 26.

two liquids may acquire the temperature indicated by the thermometer attached to the stand.

When equilibrium of temperature has been established, an excess of distilled water is poured into the apparatus, then the liquid to be studied is put into the branch, *CB*, by means of a small funnel with a point elongated and slightly curved so that it may touch the interior wall of tube, *C*. In this way the formation of any air bubbles and of any emulsion is avoided and the meniscus of separation of the

two liquids is very distinct. This meniscus is forced down into the small part, B. Then the stopcock, *D*, is cautiously opened and the water is allowed to flow out until the lower part of the meniscus of separation exactly reaches the common zero of the scale.

Attention is given to see if there is any further change in level; if it occurs it is corrected. Lastly, the heights of the two liquids above the common zero and the indication of the thermometer are read.

In the case where the bodies are more or less soluble in each other, the apparatus shown in Fig. 26 is used. In this the two liquids are separated by a column of air small enough and long enough so there can be no mingling by diffusion during the experiment.

The tubes *A*, *B*, and *C*, are arranged as before, but in place of direct communication by a simple elbow the two tubes are united by a small tube with a double elbow, having on its upper part a stopcock, *E*, with three outlets which permit connecting each of the two sections separately with the air or to connect both together, or to close them all off. The two tubes, *A* and *B*, and the two branches of the narrow tube that connects them, have a common zero mark. The two middle branches are graduated in millimeters above and below the zero mark for a distance of 50 millimeters.

To determine a specific gravity, the stopcock, *E*, is turned as is shown in Fig. 26, that is in such a way as to shut off all communication. Next, some distilled water is poured into tube, *A*, and the liquid to be studied is poured into *C* by means of the funnel described above. The cock, *E*, is now opened and an equilibrium is established. By opening either the stopcock *D* or *D'*, the two meniscuses in the small tubes can be made to stand in the graduated portion of the tubes. It is not difficult to make these

levels lower than the first level, through manipulation of the cocks, D and D', thus making sure that the capillary tension of each liquid is fully utilized. If, now, the difference in level between the free surfaces of the two liquids is measured, as in the preceding case, the heights of the two liquids in equilibrium are known, and hence their specific gravities.

Attention must be given to the fact that most of these experiments were not performed at the normal temperature of 15° C. Since in many cases foreign observations made at 15.56° C. have to be used, a temperature slightly different from the French normal temperature 15° C., the 15.56° will be used here.

For water, if t is the temperature of the experiment, the height read must be multiplied by the following coefficients to obtain the height of 15.56° C.

Temperature t.	Coefficient.	Temperature t.	Coefficient.
0° C.	1.00079	16° C.	0.99992
2	1.00087	18	0.99975
4	1.00092	20	0.99918
6	1.00089	22	0.99874
8	1.00080	24	0.99828
10	1.00075	26	0.99778
12	1.00047	28	0.99725
14	1.00022	30	0.99668

For pure methyl alcohol, the following coefficients must be used:

Temperature t.	Strength of Alcohol in Per Cent by Volume at 15.56° C.					
	100	93.17	85.47	76.94	67.69	57.70
0° C.	1.01784	1.01643	1.01498	1.01366	1.01240	1.01104
5	1.01209	1.01112	1.01015	1.00935	1.00841	1.00748
10	1.00633	1.00683	1.00531	1.00485	1.00440	1.00392
15	1.00057	1.00053	1.00048	1.00044	1.00040	1.00035
20	0.99482	0.99523	0.99565	0.99603	0.99639	0.99679
25	0.98906	0.98993	0.99081	0.99162	0.99239	0.99323
30	0.98330	0.98463	0.98598	0.98712	0.98831	0.98967

For pure alcohol the coefficients are:

Temperature *t*.	Strength of Alcohol in Per Cent by Volume at 15.56° C.					
	97	95	90	85	80	75
0° C.	1.016	1.015	1.015	1.014	1.014	1.014
5	1.010	1.010	1.010	1.010	1.010	1.009
10	1.005	1.005	1.005	1.005	1.005	1.005
15	1.0002	1.0002	1.0002	1.0002	1.0002	1.0002
20	0.995	0.995	0.995	0.995	0.995	0.995
25	0.990	0.990	0.990	0.990	0.991	0.991
30	0.985	0.985	0.985	0.985	0.986	0.986

According to Lunge the following corrections may be used for the hydrocarbons to be studied.

For Specific Gravities of 0.880 and Below.

t in Degrees C.	**2**	**4**	**6**	**8**
Subtract	0.0105	0.009	0.008	0.006
	10	**12**	**13.5**	
	0.0045	0.003	0.002	
t in Degrees C.	**15.5**	**17.5**	**19.5**	**21.5**
Add	0.0	0.001	0.0025	0.004
	23	**25**	**29**	
	0.0055	0.007	0.009	

For Specific Gravities between 0.880 and 0.920.

t in Degrees C.	**2**	**4**	**5.5**	**7**
Subtract	0.010	0.0085	0.0075	0.0065
	9	**10.5**	**12**	**14**
	0.005	0.004	0.0025	0.001

t in Degrees C.	**15.5**	**17**	**19**	**20.5**	**22**
Add	0.0	0.001	0.0025	0.0035	0.005
	24	**25.5**	**27**	**29**	
	0.006	0.007	0.008	0.0095	

FOR SPECIFIC GRAVITIES BETWEEN 0.920 AND 0.960.

t in Degrees C.	**1.5**	**3**	**4.5**	**6**	**7.5**	
Subtract	0.010	0.009	0.008	0.007	0.006	
	8.5	**10**	**11.5**	**13**	**14**	
	0.005	0.004	0.003	0.002	0.001	
t in Degrees C.	**15.5**	**17**	**18**	**19.5**	**21**	**22.5**
Add	0.0	0.001	0.002	0.003	0.004	0.005
	24	**25**	**26.5**	**28**	**29.5**	
	0.006	0.007	0.008	0.009	0.010	

Taking up again the subject of the instantaneous action of heat upon a current of vapors, when nothing to the contrary is stated, the ethyl alcohol used is 95 per cent by volume and the methyl alcohol 99 per cent.

Since it is very difficult to obtain these substances free from the corresponding aldehydes, a small quantity of acid phosphate of aniline is added to them in order to make the aldehydes enter into a non-volatile compound.

By passing air in excess with ethyl alcohol through the tube described above, it was shown that no appreciable oxidation took place until a temperature between 200 and 250° C. was reached. It should be remembered that the contact with the hot tube lasted scarcely a second. At 250° C., the condensed products began faintly to redden litmus, and the bisulphite of rosaniline showed traces of aldehyde.

At the same temperature, but in a current of carbonic acid gas, no acetic acid was observed, but a very faint trace of acetaldehyde was noticed.

It can be said that 95 per cent ethyl alcohol begins to split up at 250° C. and upwards, forming aldehyde. This is a long way from the temperature of 450 to 500° given by various authors.

In these preliminary experiments two actions might take place at the same time, that of oxygen and that of

heat. The action of oxygen was eliminated by using an atmosphere of carbonic acid gas and nitrogen.

Methyl alcohol. — Under these conditions methyl alcohol showed clear signs of decomposition at 150° C. There was found in the products coming from the condenser an appreciable quantity of formaldehyde. The potash in the spherical flask, *F*, was plainly colored yellow by the polymerization of this aldehyde drawn along by the gaseous current. The combustion in the eudiometer, of the gases collected, in very small amounts however, showed the presence of methane only. The decomposition was represented then by the simple reaction,

$$2CH_4O = CH_2O + H_2O + CH_4.$$

In subsequent experiments made at higher temperatures it was found that the quantity of formaldehyde began to diminish and that some ethylene began to be mixed with the methane at 205° C. To the principal reaction which has just been indicated there was added, even although the action continued less than a second, another reaction,

$$2CH_4O = C_2H_4 + 2H_2O.$$

Perhaps it would be better to write it

$$CH_4O = CH_2 + H_2O.$$

although the substance CH_2 does not actually exist. It will be seen that under the conditions of these experiments the radical, CH_2, attaches itself to other hydrocarbon compounds. If now the molecule is doubled we have the compound C_2H_4, whose presence has been shown. If the temperature is raised to 300° C. and above, the second reaction surpasses the first, that is to say, the production of formaldehyde diminishes as the temperature rises while the

ethylene increases. The second reaction then is the only one to consider at high temperatures in a non-oxidizing atmosphere.

However, in certain cases while working with the same apparatus the author observed a different reaction, characterized by the following equation to which reference will be made later. In the vicinity of 300° C. only traces of aldehyde were found, but the combustible gas, in a very small quantity, consisted of a mixture of methane, carbon monoxide, and hydrogen. The two following reactions must then have occurred simultaneously:

$$2CH_4O = CH_2O + H_2O + CH_4$$

and

$$CH_2O = CO + 2H.$$

At a temperature of 350° C., a much more complex reaction was found. Besides a small quantity of hydrocarbons of the acetylene series, forming a yellow precipitate with the ammoniacal copper chloride, probably C_3H_4, there were found ethylene hydrocarbons and principally some hydrocarbons of the methane series, in which ethane, C_2H_6, and propane, C_3H_8, predominated.

Ethyl alcohol. — Ninety-five per cent ethyl alcohol at a temperature of 305° C. scarcely showed any trace of aldehyde. The products not absorbed by the potash contained no combustible gases, but at 352° C., a trace of ethane with a little acetaldehyde was discovered.

$$2C_2H_6O = C_2H_6 + C_2H_4O + H_2O.$$

The breaking up of ethyl alcohol under the action of heat alone began between 300° and 350° and not at 500°, as is stated in most chemical treatises.

Since some methods of enriching the fuel mixture depend on the solubility of the light hydrocarbons of the methane

series in alcohol to which has been added some of the higher homologues of alcohol, particularly amyl alcohol, it seems well to study the action of heat on this last compound. The question would have no importance for the French denatured alcohol, since the French laws do not allow more than 1.5 per cent of essential oils in alcohol to be denatured, but the law does not contemplate the addition to denatured alcohol of hydrocarbons dissolved by the help of these essential oils.

The test was made on amyl alcohol practically pure, boiling at 130° C., evidently more pure than the commercial amyl oils. Although vaporization began at 89° C., at 255° C. only very little amylic aldehyde was found in the products condensed. There had been some in the gases, for the potash was strongly yellow. Moreover, the gases had the characteristic pungent odor of amylic aldehyde. From the contraction and the production of carbonic acid observed in the eudiometer it seemed that the formation of butane and of pentane with a trace of carbon monoxide had been shown.

At 350° the pungent odor of gases became more apparent, the presence of aldehyde seemed unquestionable, but no combustible gases were found. On the other hand, there was a slight oily yellow deposit on the walls of flask, *D*, (Fig. 24), showing that some tar-like products had been formed, heavier and but little volatile.

Formaldehyde. — Having shown that methyl alcohol produced formaldehyde at relatively low temperatures, the study of the action of heat upon this body was advantageous. Accordingly, a current of carbonic acid gas was caused to bubble through a 40 per cent neutralized solution of formaldehyde.

At 150° C. there was clearly shown the production of a combustible gas containing carbon monoxide, some acety-

lene hydrocarbons, no hydrocarbons that could be absorbed by the sulphuric acid, hence no ethylene hydrocarbons, and lastly some hydrocarbons that had resisted the action of the various absorbents of the preceding gases, and also of fuming sulphuric acid. The ratio of the contraction to the volume of the carbon dioxide resulting from its explosion in the presence of an excess of air is 0.690. As there can hardly be any question about its being a vapor of a hydrocarbon of the methane series, this hydrocarbon would have for its formula C_8H_{18}, corresponding to the ratio 0.687.

In this experiment, then, there took place a synthesis of one of the petroleum compounds forming the series which connects the commercial gasolines to kerosene.

At 350° C. the per cents of carbon monoxide and of acetylene compounds diminish. There are still no appreciable traces of hydrocarbons absorbed by the fuming sulphuric acid. The ratio of the contraction to the volume of carbon dioxide produced by the explosion in the presence of an excess of oxygen is 0.917. The methane hydrocarbons produced, which were relatively more abundant in this case than before, were then a mixture of propane, C_3H_8 (ratio 1), and butane, C_4H_{10} (ratio 0.875), in the proportions of one volume of propane for two of butane.

Hence, from the moment that formaldehyde can be formed by contact with bodies heated above 200° C., decompositions are found much more complex than in the case where only alcohol is used, in both cases no oxygen being present.

Moreover, an account might be made of the physical characteristics of the actions and the differences observed between the reactions of ethyl alcohol and methyl, and the reactions of their aldehydes.

It was observed that in these reactions no carbon was

produced at the temperature of the experiment when air was excluded. If then the molecule breaks up, the carbon present can exist only as carbon monoxide or carbon dioxide on the one hand, or as hydrocarbons on the other. Moreover, there will always be a formation of water in this incomplete combustion.

Taking up first methyl alcohol and writing the equation to express the formation of carbon dioxide, water, and a hydrocarbon,

$$nCH_4O = mCO_2 + (n - 2m)\,H_2O + C_{n-m}H_{2n+4m}.$$

Now the general formula of a hydrocarbon is C_pH_{2p+2a}. a being a number positive or negative. Hence,

$$2(n - m) = 2n + 4m - 2a$$

whence, $$3m = + a$$

for which no corresponding series exists.

The same conclusions are true in the case of ethyl alcohol.

Suppose that there could be formed carbon monoxide, water, and a hydrocarbon,

$$nCH_4O = mCO + (n - m)\,H_2O + C_{n-m}H_{2n+2m}.$$

The same reasoning as before will give the equation,

$$2n - 2m = 2n + 2m - 2a.$$

Hence, $$m = a$$

which is still impossible.

Therefore, in the absence of exterior oxygen, with the molecule of alcohol, neither carbon monoxide nor carbon dioxide can be formed.

It is, therefore, natural to infer that the carbonic oxide found in many analyses comes from the aldehydes.

Writing the equation

$$nCH_2O = mCO_2 + (n - 2m)\,H_2O + C_{n-m}H_{4m}$$

there is obtained as before,

$$2(n - m) = 4m - 2a.$$

Hence, $$n = 3m - a.$$

Supposing $$a = -1,$$

the case of the methane series. The relation

$$n = 3m + 1$$

is never satisfied.

Supposing $a = 0$, the case of the ethylene series, the relation $n = 3m$ is satisfied for integral values by

$n = 3,$	$m = 1,$	C_2H_4	ethylene
$n = 6,$	$m = 2,$	C_4H_8	butylene, etc.

All the bodies of this series, except ethylene, being easily absorbed by fuming sulphuric acid, it is evident none of them are formed under the conditions of the experiment.

Suppose, $a = +2$, the case of acetylene series. Then, $3m = n - 1$, which is satisfied for integral values by

$n = 4,$	$m = 1,$	. . . . .	C_3H_4
$n = 7,$	$m = 2,$	. . . . .	C_5H_8, etc.

Under these conditions acetylene cannot be formed, but instead its higher homologues that give a yellow precipitate when they are absorbed by ammoniacal copper chloride, which is exactly what was previously found.

On the other hand, the production of carbon monoxide has been observed.

Then $nCH_2O = mCO + (n - m)\,H_2O + C_{n-m}H_{2m}$.

As before, the relation between n and m becomes, $n = 2m - a$. Placing $a = -1$, the satisfying values are,

$n = 1$,	$m = 1$,	or H_2	. . . hydrogen
$n = 3$,	$m = 2$,	CH_4	. . . methane
$n = 5$,	$m = 3$,	C_2H_6	. . ethane
$n = 7$,	$m = 4$,	C_3H_8	. . . propane, etc.

Placing $a = 0$,

$n = 2$,	$m = 1$,	CH_2 (a radical that will be met)
$n = 4$,	$m = 2$,	C_3H_6, etc.

Placing $a = +1$,

$n = 3$,	$m = 1$, ...	C_2H_2(?)
$n = 5$,	$m = 2$	C_4H_4, etc.

The same study could be made with acetaldehyde, but it is less interesting, since much higher temperatures are required to decompose ethyl alcohol. It is, however, well to note the reaction,

$$C_2H_6O = CH_2O + CH_4$$

which explains the formation of formaldehyde in some imperfect combustions at the cost of ethyl alcohol.

Before leaving the main question it will be well to see what takes place when a hydrocarbon, benzene for example, is combined with the substances just studied.

Alcohol and benzene. — If there is passed into the tube at 300° C. a mixture obtained by bubbling carbon dioxide through ethyl alcohol mixed with 10 per cent of benzene and heated to 50° C., as has been previously seen, there are very nearly equal parts of alcohol and of benzene in the

vapor. Under these conditions hardly anything but benzene vapor is found in the gas not condensed. No reaction has taken place.

If the temperature is raised to 350° C., less gas seems to form; a small part is absorbed by the fuming sulphuric acid and by the ammoniacal copper chloride. The residue gives a ratio of contraction to the carbon dioxide formed equal to 1.361, which corresponds to a mixture of methane and ethane. Lastly, the liquid hydrocarbons collected in the vertical cooling tube, and freed from alcohol, have the odor of crude benzol and a specific gravity of 0.875. Hence they contain some toluene. These reactions can be explained by the following theoretic formulae:

$$C_6H_6 + C_2H_6 = 2C_4H_6$$
$$\begin{cases} C_2H_6 = CH_4 + CH_2 \\ C_6H_6 + CH_2 = C_7H_8. \end{cases}$$

On repeating the same experiment with a mixture of methyl alcohol and 10 per cent of benzene at 300° C., there was shown the presence of carbon monoxide and an acetylene hydrocarbon that formed a yellow precipitate with copper chloride. After absorbing the traces of benzene vapor by fuming sulphuric acid, a small amount of hydrogen and of methane were found. These are the usual residues from the decomposition of formaldehyde. The benzene appeared not to be changed, at least the part of it that could be extracted by the vertical condenser had a specific gravity of 0.888 at + 10° C., or 0.884 at 15° C.

At 350° C. only benzene vapor was found in the eudiometer. Hence the direct products of the decomposition of methyl alcohol have disappeared. On the other hand, the hydrocarbon collected in the vertical condenser had a specific gravity of 0.880 at + 10° C., or nearly 0.876 at 15° C. Hence a great part of it is formed of toluene.

There is then the reaction.

$$\begin{cases} CH_4O = CH_2 + H_2O \\ C_6H_6 + CH_2 = C_7H_8. \end{cases}$$

Alcohols and gasoline. — On substituting gasoline for benzene in the above mixture at 250° C., there were produced acetylene hydrocarbons and a trace of hydrocarbons absorbed by fuming sulphuric acid. What remains of the combustible gases shows at the time of the combustion a ratio of contraction to the carbonic acid gas formed by combustion equal to 0.810, corresponding very nearly to pentane, but the products condensed have a specific gravity increased to 0.730 at 13.2° C. (the initial mixture of hydrocarbons had a specific gravity of 0.687 at 13.8° C). This specific gravity, corresponding to a mixture of nonane and of decane, is such that it must be concluded that the small quantity of gas recovered represents all that remains of the lighter portions of the petroleum series. Hence there is reason to think this reaction is like the preceding, that is, a decomposition of methyl alcohol and a fixation of the radical, CH_2, upon the molecule of a methane hydrocarbon.

Formaldehyde and hydrocarbons. — With a mixture of formaldehyde and one fourth its volume of benzene, there was observed at 250° C., the presence of the hydrocarbon homologues of acetylene, ethylene hydrocarbons, but no carbon monoxide. The ratio of contraction to carbon dioxide after combustion is 1.81. Hence it is probable that there is present some methane naturally mixed with benzene. The benzene has not been changed in composition, for the portion collected in the vertical condenser had a specific gravity of 0.886 at 12.4° C., or 0.884 at 15.5° C. On repeating the same experiment at 350°C, a complete

change was observed. The predominating gases were carbon monoxide and the homologues of acetylene (probably allylene), no hydrocarbons rapidly absorbed in fuming sulphuric acid, traces of a methane hydrocarbon, and benzene vapor. The benzene was not perceptibly changed, for the portion of the product, insoluble in water, that was collected in the vertical condenser had a specific gravity of 0.886 at 11.5° C., or 0.883 at 15.5° C.

Next, on studying the action of 300° C. on a mixture of formaldehyde and gasoline, no carbon monoxide nor acetylene hydrocarbons were found. There was a trace of hydrocarbons rapidly absorbed in fuming sulphuric acid. The other combustible gases which exploded with great violence consisted almost exclusively of hexane vapor. The portion of the product condensed, insoluble in water, had as its specific gravity 0.716 at 15.5° C. Hence it probably was octane.

At 350° C.carbon monoxide and the acetylene homologues predominated, as they did in the experiment with benzene. There were no ethylene hydrocarbons. Naturally there were present gasoline vapors. The portion of the product condensed, insoluble in water, had as its specific gravity 0.702 at 10.5° C. Hence it is principally a mixture of heptane and hexane.

To sum up, in the cases in this first series of studies where the vapors are, for less than a second, and without the presence of oxygen, raised to a temperature of 350° C. in the presence of solid bodies without effect upon them, methyl alcohol is the only one capable of transforming a hydrocarbon into its less volatile higher homologues. This corresponds to the formation of tar-like substances upon the exterior of certain admission valves.

Amyl alcohol of fermentation can also furnish a little of these substances, but it is hardly to be taken into account,

since, according to the laws for denaturing, only a negligible per cent can be present.

Ethyl alcohol and formaldehyde, either alone or mixed with benzene, or with the hydrocarbons of the methane series, present under the above conditions only the inconvenience of being partially transformed into gases still combustible, but in which a part of the carbon has been already burned, and which, moreover, cannot mingle in a homogeneous manner with the residue of the charge.

CHAPTER XI.

THE SLOW ACTION OF TEMPERATURES RELATIVELY LOW ON THE VAPORS OF THE ALCOHOLS OR THEIR DERIVATIVES.

To increase the length of time the gas remained in the warm chamber, a Bohemian glass tube having an interior diameter of 16 millimeters was substituted for the narrow tube used in the previous experiments; and in order that all the gaseous layers should be equally warmed the part of this tube which was immersed in the hot air bath was filled with fragments of porcelain. It is clear that the vapors, as soon as they reached one of the temperatures observed in the preceding experiments, would begin to undergo the same instantaneous reactions. But there might arise among the new compounds formed some new reactions to complicate the results. It was important to verify this point in order to know whether the same phenomena will take place on the surface of admission valves in high speed engines and in relatively slow engines. Since the gas remained longer in the hot tube there was a chance for an analysis of greater volumes of gas than in the preceding experiments.

Methyl alcohol. — Two experiments were made at 350° C. with methyl alcohol quite free from aldehyde; the first corresponds to a slow passage of the vapors, the other to a speed about twice as great.

In the first case neither carbon monoxide nor acetylene hydrocarbons were found. There was a small amount of hydrocarbon absorbable in fuming sulphuric acid. Much

the greater part of the combustible gases consisted of pure hydrogen.

Much formaldehyde was formed. The liquid condensed was neutral, and has a specific gravity of 0.786 at 19° C., or 0.789 at 15.5° C. This specific gravity is remarkably low, for 99 per cent alcohol has a specific gravity of 0.799. The same result will often be found when the production of aldehyde is large.

Consequently the principal reaction will be,

$$CH_4O = CH_2O + H_2.$$

In the second experiment there was very little aldehyde. However, the usual collection of derivatives of formaldehyde was present, carbon monoxide, acetylene hydrocarbons, and ethane, as well as some ethylene which is the leading component. The specific gravity of the liquid condensed was 0.778 at 15.1° C.

Ethyl alcohol. — With ethyl alcohol besides the influence of temperature that of dilution was studied.

The vapors of 95 per cent alcohol formed at 65° C. submitted to the temperature of 250° C. produced aldehyde, carbon monoxide, and allylene. The residual liquid had a neutral reaction, and its specific gravity was 0.798 at 15.2° C. At 350° C the proportion of aldehyde materially increased. The gases formed were carbon monoxide, allylene or one of its higher homologues, some hydrocarbons absorbable in fuming sulphuric acid, and a mixture of ethane and ethylene in which ethane predominated. The liquid condensed had a decided acid reaction with litmus. Its specific gravity was 0.787 at 21° C. At this temperature the specific gravity of 95 per cent alcohol would have been 0.8223.

For the first time the production of an acid is found. It probably can be explained by the formulae,

$$2C_2H_4O = C_2H_4O_2 + C_2H_4$$

or,

$$2C_2H_6O = C_2H_4O_2 + C_2H_4 + 4H,$$

the hydrogen reacting on the ethylene hydrocarbons to make a methane hydrocarbon.

Ninety per cent alcohol at a temperature of 350° C. gave a volume of gas more abundant than in the case above. The gases left on the potash a yellow oily liquid in too small a quantity to be studied.

The liquid condensed was very acid and contained no body insoluble in water. Its specific gravity was 0.796 at 19° C. (at this temperature the specific gravity of 90 per cent alcohol would have been 0.837). Less aldehyde was found than in the preceding case.

The combustible gases consisted of small amounts of carbon monoxide and of ethylene hydrocarbons associated with a small amount of compounds such that their ratio of contraction to the volume of carbon dioxide produced by combustion is 0.513. This ratio is practically that which belongs to the hydrocarbons of the form C_nH_{2n-4}, perhaps the pyropentaline C_5H_6 which boils at 42° C. and would be the oily substance observed on the potash.

Since 85 per cent ethyl alcohol is used in Germany, that was also studied. The experiment was made at 350° C. Consequently, aldehyde was produced abundantly. The liquid condensed had a specific gravity of 0.813 at 17.4° C., corresponding to 95 per cent ethyl alcohol at 15° C. The acidity was quite weak. The gases produced contained no acetylene hydrocarbons. There was found carbon monoxide, a small amount of hydrocarbons absorbable in fuming sulphuric acid, and especially methane and ethane.

Formaldehyde. — A solution of 40 per cent formaldehyde perfectly neutralized was used under the same conditions at a temperature of 346° C. The liquid condensed turned litmus red like strong acids.

The gases contained carbon monoxide, and some acetylene hydrocarbons. Fuming sulphuric acid showed an increase of volume, due, without doubt, to the decomposition of a small amount of aldehyde vapor incompletely polymerized by the potash. According to this reaction a very appreciable amount of carbon monoxide was found. A little propane and butane were also present.

Alcohols and benzene. — Methyl alcohol mixed with 10 per cent of benzene was heated to 50° C. and the vapors given off were submitted to a temperature of 350°C. The pure benzene used had a specific gravity of 0.884 at 15.5° C. The hydrocarbon obtained from the residual liquid collected in the vertical condenser had a specific gravity of 0.898 at 14.2° C., or 0.897 at 15.5° C.

A small amount of benzene was condensed in the potash.

The gases contained neither carbon monoxide nor acetylene, very little ethylene hydrocarbons, except a considerable amount of ethylene, and naturally they were saturated with benzene vapor.

Formaldehyde and benzene. — Lastly an experiment was made on a mixture of neutral formaldehyde and benzene. The vapors were submitted to a temperature of 350° C. Naturally there was found a very strong acidity in the condensed liquid. The hydrocarbon extracted from this liquid had a specific gravity of 0.871 at 16.5° C. It was, then, almost pure benzene. For the first time some very fine carbon appeared. There were present neither carbon monoxide nor acetylene compounds, a very small amount of hydrocarbons absorbable in sulphuric acid, and a little ethylene. Consequently, the acidity that is found in the

products of combustion in alcohol engines may come from the reactions taking place in the hottest parts of the carbureter away from the air. Methyl alcohol is only indirectly responsible for the acidity. It gives off acid when it is decomposed in such a manner as to form much formaldehyde.

Ethyl alcohol normally produces acid. It is, though, formaldehyde which is the source of the most dangerous acidity, and since methyl alcohol produces formaldehyde, sometimes in considerable amount, methyl alcohol in large quantities is to be avoided.

CHAPTER XII.

SIMULTANEOUS ACTION OF HEAT AND OXYGEN.

In the preceding studies it has been supposed that the combustible liquids were suddenly projected upon a hot surface, that they were instantly vaporized and decomposed, thus forming a sort of cushion between the mixture of vapors and oxygen, and the hot surface, an intermediate zone containing but little oxygen.

If such a case can exist, and certainly it does, two conditions can be imagined. In the first the vapors set free are diffused into the mixture of air and explosive vapors. In the second, the gases set free from contact with the hot valves are first drawn into the residual gases in the compression chamber. These are relatively weak in oxygen, according to the author's experiments on engines made at the French international tests in 1902. These gases are heated by compression without any intimate mixing taking place during the compression stroke.

Method of experimenting. — In order not to complicate the study and to apply investigations to the two cases proposed, an attempt was made to keep the amount of oxygen in the gases between the limits of 4 and 5 per cent, an amount compatible with the conditions of satisfactory action as shown by the experiments at the French Competition in 1902.

A reaction water motor worked some Schloesing intermittent compression pumps in such a manner as to produce approximately the desired mixture. Two pumps drew in carbon dioxide, a third the air, and the mixture was forced

into a large bottle before passing to be purified into the tube containing calcium chloride and calcium carbonate. A stopcock was placed at the exit of the chloride of calcium tubes which permitted an average sample to be obtained of the gaseous mixture bubbled through the combustible liquid. Otherwise the apparatus was arranged as described before.

Air and methyl alcohol. — Some 99 per cent methyl alcohol was heated to 50° C., and there was caused to bubble through it a gaseous current composed of 77.54 per cent of carbon dioxide and 22.46 per cent of air. Consequently the mixture contained 4.49 per cent of oxygen. The mixture of gas and vapors was raised to 160° C. The condensed liquid was very acid, and its specific gravity was 0.881 at 17.2° C.

After the absorption of the carbon dioxide by the potash, the residual gas contained 20.35 per cent of oxygen, 1.07 per cent of carbon monoxide, 0.25 per cent of acetylene hydrocarbons, no other hydrocarbons absorbable by the sulphuric acid, 0.42 per cent of ethylene, 0.21 per cent of methane. The nitrogen found by subtraction was 77.70 per cent. Referred to 79.2 per cent of nitrogen, the normal amount in the air, the oxygen found amounts to 20.70 per cent in place of 20.80. Hence a little oxygen had been consumed. The gases found came principally, then, from the decomposition of aldehyde.

The same experiment was repeated at 200° C. The oxygen in the gases before bubbling was 4.89 per cent. The condensed liquid was scarcely acid, and its specific gravity was 0.752 at 17.4° C.

The gases collected consisted of:

Oxygen	17.61
Carbon monoxide	0.73
Acetylene hydrocarbons	1.03
Hydrocarbons absorbable in sulphuric acid	0.63
Nitrogen	80.00
	100.00

Consequently a combination of oxygen had taken place, for the ratio of oxygen to nitrogen was $\frac{17.43}{79.20}$ in place of $\frac{20.80}{79.20}$. Hence 16.3 per cent of the oxygen introduced had combined.

In the third experiment where the oxygen in the gases before bubbling was 4.58 per cent, the temperature was raised to 350° C. The condensed liquid was almost neutral, and its specific gravity was 0.787 at 17.5° C.

The gases collected over the potash were:

Oxygen	15.73
Carbon monoxide	1.72
Acetylene hydrocarbons	3.02
Hydrocarbons absorbable in sulphuric acid	traces
Nitrogen	80.53
	100.00

In place of the normal ratio of oxygen to nitrogen, $\frac{20.80}{79.20}$, there was only $\frac{15.58}{79.20}$. Hence the consumption of oxygen had increased and 25.1 per cent of the oxygen intro-

duced had combined. Therefore, when methyl alcohol is made to react instantaneously on gases very poor in oxygen like those which result from a normal explosion in an engine, the oxidizing action begins at about 160° C., and increases rapidly in intensity as the temperature rises. The same action takes place for a slight distance from the admission valves if there has been any methyl alcohol projected upon these valves. In both cases there is loss of energy, since combustion has taken place before explosion. However, it is to be noticed that the objection of acidity presents itself only at relatively low temperatures.

Air and ethyl alcohol. — The vapor furnished by 95 per cent ethyl alcohol was treated in the same way at a temperature of 250° C. in a gaseous current containing 4.74 per cent of oxygen. The condensed liquid was neutral and had a specific gravity of 0.813 at 14° C. The gases collected over the potash contained, besides a trace of ethylene, 18.50 per cent of oxygen. Hence there had been combustion of alcohol at 250° C.

The vapors furnished by 95 per cent alcohol in a bath having a temperature of 76° C., were submitted to a temperature of 354° C. in a gaseous current containing 4.03 per cent of oxygen. The condensed liquid had a specific gravity of 0.822 at 14° C. It was slightly acid. The gases contained a trace of ethane. No oxygen was consumed.

Air and formaldehyde. — Vapor formed at 65° C. by a 40 per cent neutral solution of formaldehyde diluted in a gaseous mixture containing 4.98 per cent of oxygen, gave after heating to 200° C. a very slight amount of condensed liquid that was but little acid. The gases collected over the potash contained:

Oxygen	19.71
Carbon monoxide	0.86
Acetylene hydrocarbons	0.66
Ethylene hydrocarbons	0.10
Nitrogen	78.67
	100.00

The ratio of oxygen, 19.71 + 0.43 = 20.14, to nitrogen is $\frac{20.27}{79.20}$, in place of $\frac{20.80}{79.20}$. Consequently oxygen had been consumed in the proportion of 2.55 per cent to form water or carbon dioxide, and in addition 2.07 per cent to form carbon monoxide.

The same experiment was repeated with the aldehyde heated to 70° C. in a current of gases containing 6.97 per cent of oxygen. The vapor obtained was heated to 330° C. The condensed liquid was very acid. The gases collected over the potash contained:

Oxygen	19.72
Carbon monoxide	0.68
Acetylene hydrocarbons	0.98
Ethylene hydrocarbons	0.55
Nitrogen	78.18
	100.00

The ratio of oxygen, 19.72 + 0.34 = 20.06, to nitrogen is $\frac{20.31}{79.20}$, almost exactly as before. Hence, the same conclusions may be drawn.

Before entering upon the study of enriched alcohol mixtures, a study will be made of what takes place with the enriching agents alone.

Air and benzene. — Some purified benzene was heated to 60° C. in a current of gas containing 6.25 per cent. of oxygen. The resulting gases were submitted to a temperature of 350° C. There was no condensed liquid, but a very slight amount of dark smoke was observed.

The gaseous mixture contained:

Oxygen	18.92
Carbon monoxide	0.71
Acetylene hydrocarbons	1.10
Ethylene hydrocarbons	0.69
Nitrogen	78.59
	100.00

The ratio of oxygen, 18.92 + 0.35 = 19.27, to nitrogen is $\frac{19.42}{79.20}$, in place of $\frac{20.80}{79.20}$. Hence more loss of energy had taken place than in the case of alcohol.

The same experiment was repeated by heating the benzene to 70° C. in the gaseous current containing 4.73 per cent of oxygen. The resulting gases were then heated to only 250° C. The condensed liquid was slightly yellowish. Its specific gravity at 28.5° C. was 0.875, or 0.884 at 15.5° C. Hence the liquid was unchanged benzene.

The gases collected over the potash contained:

Oxygen	19.50
Carbon monoxide	0.42
Acetylene hydrocarbons	1.68
Methane (?)	traces
Benzene vapors	2.88
Nitrogen	75.52
	100.00

The ratio of oxygen, 19.50 + 0.21 = 19.71, to nitrogen is $\frac{20.67}{79.20}$. Hence almost the entire amount of oxygen is found either as free oxygen or as carbon monoxide.

Air and gasoline.—In order to make a comparison with gasoline engines, the author heated some gasoline having a specific gravity of 0.704 at 22.8° C. or 0.709 at 15.5° C. to a temperature of 50° C. in a current of gas containing 4.63 per cent of oxygen. The mixture was submitted to a temperature of 350° C. The condensed liquid had a specific gravity of 0.692 at 22.8° C., or 0.697 at 15.5° C.

The gas collected over the potash contained:

Oxygen	14.27
Carbon monoxide	0.51
Acetylene hydrocarbons	1.62
Ethylene hydrocarbons	3.29
Propane	22.20
Butane and its homologues	traces
Nitrogen	58.02
	100.00

The ratio of the oxygen, 14.27 + 0.25 = 14.52, to nitrogen is $\frac{19.82}{79.20}$, in place of $\frac{20.80}{79.20}$. Hence water or carbon dioxide had been formed consuming 4.71 per cent of the oxygen introduced. A small amount of carbon monoxide had also been formed.

The same experiment was repeated with gasoline of the same specific gravity heated to 50° C. in a current of gas containing 5.72 per cent of oxygen. The mixture was in this case heated to only 250° C.

The condensed liquid, as well as the potash, was clouded with soot. The specific gravity of this condensed liquid was 0.684 at 22.5° C., or 0.699 at 15.5° C.

Air and kerosene. — To complete the comparison the author experimented on common commercial kerosene. In the first experiment this oil was heated to 81° C. in a current of gas containing 4.83 per cent of oxygen, and the resulting mixture was heated to 250° C. The amount of soot formed was so slight as to be found only upon the glass beads in the potash flask.

The gas collected over the potash contained:

Oxygen	19.34
Carbon monoxide	0.37
Ethylene hydrocarbons	0.26
Tredecane	2.45
Nitrogen	77.58
	100.00

The ratio of the oxygen, 19.34 + 0.18 = 19.52, to nitrogen is $\frac{19.92}{79.20}$, in place of $\frac{20.80}{79.20}$. Hence before explosion 4.23 per cent of oxygen would have been used up, with a consequent loss of energy.

In the second experiment a temperature of 350° C. was used. The initial gaseous mixture contained 4.84 per cent of oxygen. There was still observed the production of a very slight amount of soot.

The gas collected over the potash contained:

Oxygen	19.87
Carbon monoxide	0.29
Ethylene hydrocarbons	0.13
Butane	1.22
Pentane	1.20
Nitrogen	77.29
	100.00

The ratio of oxygen, 19.87 + 0.15 = 20.01, to the nitrogen is $\frac{20.50}{79.20}$, in place of $\frac{20.80}{79.20}$. Hence there had been but little oxygen consumed uselessly. Consequently the formation of soot is attributable not to incomplete combustion, but to a commencement of *cracking*, shown by the appearance of the light hydrocarbons of the methane series.

Air and carburated alcohol. — The study of mixtures used in alcohol engines is taken up again to see if the enriching of the alcohol plays any important part in the reactions that take place before the explosion.

A neutral mixture of methyl alcohol and 10 per cent of benzene was heated to 55° C. in a current of gas containing 5.23 per cent of oxygen. This mixture was heated to 250° C. Nothing was found in the condensed liquid. The gas collected over the potash contained:

Oxygen	19.18
Carbon monoxide	0.75
Ethylene hydrocarbons	0.35
Ethylene	traces
Benzene	5.59
Nitrogen	74.13
	100.00

The ratio of the oxygen, 19.18 + 0.37 = 19.55, to nitrogen is $\frac{20.88}{79.20}$. Here is a small error giving too much oxygen, due, without doubt, to the presence of benzene whose specific gravity when cold is much greater than the theoretic specific gravity. This causes the volume of nitrogen, found by subtraction, to be too small.

To sum up the result of the experiment, from the point of view under consideration, shows that no harm arises from adding benzene to the alcohol.

CHAPTER XIII.

ACTION OF METALS IN THE ABSENCE OF FREE OXYGEN.

Introductory. — Recent investigations show that the presence of certain metals plays an important part in the transformation of various combustible bodies.

R. Schenck and F. Zimmermann (*Ber.* 1903, 36 (6) 1231–1251) studied the reversible reaction, $2CO \rightleftarrows C + CO_2$, and showed that at a relatively low temperature it could take place in the presence of finely divided metals such as iron, nickel, and cobalt.

They recall that recently Boudouard (*J. of Ch. Ind.*, 1889, page 767; 1890, page 806, 1899, pages 278, 279, 498, 782; 1900, page 1196) described the conditions under which this reaction is most rapid, and showed that the presence of oxides of these metals hastens the reaction. At 445° C. carbon monoxide in contact with them is almost entirely changed into carbon dioxide without change of volume. There is no production of carbon but reduction of the oxides.

On the contrary, in contact with finely divided metals, there is production of carbon and the volume of the gases is reduced approximately to a half of its original amount.

It seems according to this that the reaction is bimolecular, and is expressed by the relation

$$2CO = C + CO_2.$$

At lower temperatures the reaction would be unimolecular and expressed by

$$CO = C + O$$
$$CO + O = CO_2.$$

The inverse reaction,

$$CO_2 = CO + O$$

might take place under suitable conditions.

The peculiarity of unimolecular reaction is that the pressure can be lowered below half the original pressure and approach zero pressure, all the carbon monoxide being turned into carbon. According to the above authors, this is what takes place in the presence of nickel or of cobalt.

In the case of iron, the reaction would be unimolecular at 445° C and would become bimolecular at 508° C. Schenck and Zimmermann consider as incorrect the formula,

$$2Fe + 3CO = Fe_2O_3 + 3C$$

because there is proven the simultaneous presence of CO and CO_2.

Sabatier and Senderens (*Bull. S. Ch.*, 1903, 29) took up this study by heating the finely divided metals in glass tubes, over 35 centimeters long and less than 8 millimeters thick, first in hydrogen until the desired temperature was reached, then in carbon monoxide apart from the air. They measured the intensity of the reaction by comparing the velocity of entrance and of exit of the gas and by analyzing the gases collected. They found that with pure nickel at 230° C. and above there was a deposit of carbon, but that it is useless to raise the temperature between 230° and 400° C., to increase the surface of the nickel or diminish the speed of the current of gas. They were unable to realize completely the bimolecular reaction,

$$2CO = C + CO_2.$$

On the other hand, at high temperatures neither nickle nor its mixture with carbon reduces carbon dioxide.

Beginning at 300°C, cobalt acts like nickel.

Below 100° C. iron gives ferro-carbonyl. From 100° C. to 200° nothing is produced. About 330° C. the following reaction begins,

$$Fe + CO = FeO + C.$$

Above 400° C. is found the following

$$FeO + CO = Fe + CO_2.$$

Above 450° C, the two reactions have an increasing rapidity. However, the first is always superior to the second. Moreover, since at this temperature iron does not react upon carbon dioxide, some iron closed in a jar with carbon monoxide changed it entirely into carbon and carbon dioxide.

Coming now to the case of the alcohols and their hydrocarbons, Iahn (*Ber.*, vol. xiii, page 987) showed that between 300° C. and 350° C. alcohol in the presence of powdered zinc gave ethylene and water. That at dull red heat it produced carbon monoxide, hydrogen, and methane. Ipatjev (*Ber.*, 1901, pages 596 and 3579; 1902, pages 1047 and 1057) found that alcohol heated to 600° C. decomposed into aldehyde and hydrogen (the author found that the reaction took place very much sooner), that at a higher temperature in the presence of iron much carbon was produced.

According to Ipatjev there was no reaction with copper. This statement is denied by Sabatier. Besides, it will be seen that a small quantity of a foreign body alloyed with the acting metal is sufficient to change the reactions greatly. According to Sabatier, from 200° C. in the presence of copper, alcohol produces pure hydrogen and aldehyde. At 330° C. there is formed in addition to the hydrogen and aldehyde a small amount of acetal. At 440° C. a part of the aldehyde gives methane and carbon monoxide. No carbon is formed.

With nickel the reaction begins at 150° C., it is marked at 178° C., then diminishes beyond 250° C. Aldehyde is formed during the reactions. At 178° C. the gases are made up of 23 volumes of carbon monoxide, 29 volumes of methane and 48 volumes of hydrogen.

At 230° C. nickel changes carbon monoxide into carbon and carbon dioxide. The phenomenon is very marked at 330° C., and the composition of the mixture is found to be 19 volumes of carbon dioxide, 60.7 volumes of methane, and 19.8 volumes hydrogen.

At 310° C. platinum produces very little aldehyde and acetal; there is no separation of carbon. The gaseous mixture produced is made up of 30 volumes of carbon monoxide, 30 volumes of methane, and 40 volumes of hydrogen.

The author tried these experiments at about 350° C., using a small amount of finely divided metal contained in a procelain boat placed in the hot part of a large Bohemian tube. The mixture of carbon dioxide and vapors had been heated before reaching the metal, in the rear part of the tube which contained fragments of porcelain. Thus the contact of the vapors with the metal was very short. The vapors were diluted at will to a mixture of constant composition.

These differed from the preceding experiments in that the action of heat was added to the action of the metal. From the point of view of the present research this is rather an advantage, for the two actions take place simultaneously also in engines.

Action of soft iron filings. — Before starting on the study of alcohol, pure or enriched, the pure benzene must first be studied. This body was heated to 71° C., and the mixture of its vapors and carbon dioxide was submitted to a temperature of 350° C.

The liquid collected in the condenser had a specific gravity of 0.877 at 21.6° C., or 0.881 at 15.5° C. Hence it was no longer pure benzene. Over the potash in the flask there floated a thin, oily layer of a substance soluble in water, too small in amount to have its composition determined. The filings of soft iron had slightly increased in weight, but a layer of carbon had stuck together the upper part of the filings, while the under part was unchanged. Hence the reaction stopped before the end of the experiment.

The combustible gas collected over the potash was composed of a small amount of ethylene and of acetylene hydrocarbons with a trace of methane and some benzene vapor.

Soft iron filings and alcohol. — Next there was studied the action of soft iron filings on 95 per cent ethyl alcohol at a temperature of 350° C. A small amount of carbon was formed that was carried along by the gaseous current. The metal did not change in weight. It simply changed color and turned blue and yellow.

The specific gravity of the liquid condensed was 0.790 at 23° C. This liquid contained much aldehyde, but no acid. The gas contained neither carbon monoxide nor acetylene hydrocarbons, but did contain some ethylene hydrocarbons, and above all some ethane and some hydrogen.

Ethylene hydrocarbons	3.10
Ethane	49.91
Hydrogen	47.13
	100.14

So during this very short contact, the carbon monoxide disappeared and carbon appeared, while hydrogen and aldehyde were very abundant.

The same experiment was repeated with 99 per cent methyl alcohol at a temperature of 350° C. The iron used in the former experiment was used again to see if the slight change it had undergone would increase. This time, as before, the iron did not change in weight, but its surface became dull. Aldehyde was still obtained, but no acid. The liquid condensed had for its specific gravity 0.783 at 26.2° C.

The combustible gases collected over the potash were composed of:

Carbon monoxide	0.67
Acetylene hydrocarbons	0.73
The higher ethylene hydrocarbons	2.83
Ethylene	1.42
Ethane	25.02
Hydrogen	69.46
	100.13

The proportion of hydrogen actually formed should be greater, for the ethane is probably derived from the reaction of the hydrogen upon the ethylene, which, at this temperature, is the direct result of decomposition of methyl alcohol upon the action of heat.

Soft iron filings and formaldehyde. — The same iron was used with formaldehyde vapor at 350° C. Much gas was formed. The liquid condensed was very acid. The weight of the iron was not changed.

The combustible gases collected over the potash consisted of:

Carbon monoxide	1.40
Acetylene hydrocarbons	1.63
Ethylene	2.94
Ethane	13.44
Hydrogen	80.58
	99.99

Soft iron filings and carburated alcohol. — A mixture of 99 per cent methyl alcohol with 10 per cent of benzene was submitted to a temperature of 300° C. The weight of the iron increased 1.5 milligrams, due doubtless to the partial decomposition of the benzene. There was little aldehyde formed but great acidity.

The combustible gases collected over the potash consisted of:

Acetylene hydrocarbons	0.41
Ethylene hydrocarbons	10.65
Ethylene	11.08
Ethane	12.19
Hydrogen	65.69
	100.02

In the next experiment the same vapors were heated to 350° C. The hydrocarbon obtained from the condensed liquid had a specific gravity of 0.868 at 29.6° C., or 0.877 at 15.5° C. Hence it was toluene, as had been observed previously. The iron had increased less in weight but carbon had been carried over into the potash.

The combustible gases collected over the potash consisted of:

Acetylene hydrocarbons	0.18
Ethylene hydrocarbons	1.57
Ethylene	12.66
Ethane	25.89
Hydrogen	59.80
	100.10

Finally, a mixture of the vapors of formaldehyde and benzene was heated to 350° C. As before, there was a very small increase in weight of the iron, but still carbon was carried into the potash. The condensed liquid was very

acid, and the hydrocarbon obtained from it had a specific gravity of 0.871 at 26.2° C., or 0.878 at 15.5° C. It was, then, still toluene.

The combustible gases collected over the potash consisted of:

Acetylene hydrocarbons	0.74
Ethylene hydrocarbons	0.29
Ethylene	10.78
Benzene	3.17
Hydrogen	85.00
	100.18

Thus, the author observed, as in the experiments of Sabatier, the more or less complete disappearance of carbon monoxide, remarkable in the present experiments because of the short time of contact.

There was a very considerable production of hydrogen, as Sabatier had found.

On the other hand, except in the case where benzene was used, no weighable quantity of free carbon was found.

The same mass of iron served for all these experiments on alcohol. It was stated that after the second experiment the metal commenced to tarnish. This oxidation continually increased. After the last experiment, the physical condition of the iron was so much changed that the metal could be powdered in a porcelain mortar. The resulting product was reduced iron. First oxidation had taken place and then reduction. But the absence of carbon would tend to show that the reduction was due to carbon and not to carbon monoxide.

Turnings of gray cast iron. — Naturally soft iron is not suited for making valves and cylinders; it can serve only as the beginning point of these experiments. Hence the common metals were next employed, gray cast iron and

tool steel. Vapor of 95 per cent alcohol heated to 350° C. with cast iron produced a large amount of aldehyde, but very little acid. Under the microscope a deposit of carbon was found upon the metal as well as on the exposed walls of the boat. This carbon seemed to be granular. The condensed liquid had a specific gravity of 0.802 at 21.3° C.

The combustible gases collected over the potash consisted of:

Carbon monoxide	4.45
Ethylene	7.26
Ethane	6.79
Hydrogen	81.50
	100.00

On substituting 99 per cent methyl alcohol for ethyl alcohol in the above experiment, a relatively small amount of aldehyde was formed, but the liquid condensed was very acid. The formation of gas is obviously slower than in the former case. Much carbon was deposited at the front end of the boat (exposed to the current of gas). This phenomenon will be met several times in the following experiments as if a limited reaction or an apparent equilibrium had taken place. This carbon is thick as is that upon the walls of the boat. None was carried over in a state of smoke, as was the case with soft iron. The combustible gases collected over the potash were composed of:

Carbon monoxide	19.41
Acetylene hydrocarbons	0.94
Ethylene	traces
Ethane	16.36
Hydrogen	63.28
	99.99

Formaldehyde vapor was used under the same conditions. A rapid production of gas was observed. The small amount of liquid condensed was very acid. Carbon was deposited all over the iron but especially on the end as well as upon the walls of the boat.

The combustible gases collected over the potash were composed of:

Carbon monoxide	2.21
Ethane	9.41
Hydrogen	88.38
	100.00

As is seen, cast iron did not act in the presence of carbon monoxide like pure iron. It seemed rather to increase the production of carbon monoxide at the expense of the alcohols, especially methyl alcohol. The hydrogen could not come entirely from a decomposition of alcohol into hydrogen and aldehyde, since formaldehyde produces it in large amounts.

Turnings of tool cast steel. — The turnings of cast iron were replaced by those of cast steel at a temperature of 350° C. and the vapor of 95 per cent ethyl alcohol was passed over them. No carbon was formed. Much aldehyde was produced but no acid. The surface of the metal was slightly darkened but kept its polish. The liquid condensed had a specific gravity of 0.799 at 21° C.

The combustible gases collected over the potash were composed of:

Carbon monoxide	0.60
Ethylene hydrocarbons	1.41
Ethylene	7.05
Ethane	3.95
Hydrogen	86.98
	99.99

Under like conditions the vapor of methyl alcohol gave but little aldehyde. A small amount of acid was formed. The liquid condensed had a specific gravity of 0.793 at 19° C. It had an unpleasant odor that would have been repulsive if it had been further developed. A very small quantity of carbon appeared in the first quarter of the boat.

The combustible gases collected over the potash were composed of:

Carbon monoxide	2.14
Ethylene	2.41
Ethane	12.33
Hydrogen	83.11
	99.99

So the presence of a small amount of carbon combined with the iron disguises or overcomes the reaction of the iron on the carbon monoxide. The amount of hydrogen formed is always large, so much so as to make this gas predominate in the products of the decomposition.

Iron and nickel are the only metals used in engines in contact with alcohol vapor at high temperatures. However, in order to try to grasp the nature of these reactions, the author also studied aluminum and zinc.

Aluminum. — At a temperature of 350° C. in the presence of ethyl alcohol vapor, pure aluminum increased much in volume, and was changed into a gray powder, a mixture of aluminum not yet attacked, alumina, and carbon. Large quantities of aldehyde were formed, and the liquid condensed was very acid. Gas was produced abundantly.

The combustible gases collected over the potash consisted of:

Ethylene hydrocarbons	5.10
Ethylene	11.55
Ethane	14.50
Hydrogen	68.84
	99.99

The same experiment tried with methyl alcohol at 350° produced a very large amount of gas. There was noticeably less aldehyde than in the preceding experiment. The liquid condensed was neutral. The metal increased in volume as before, and gave a porous mass composed of a residue of aluminum not attacked, some alumina, and some carbon.

The combustible gases collected over the potash contained:

Carbon monoxide	0.72
Ethylene	0.68
Ethane	17.24
Hydrogen	81.35
	99.99

The same experiment was repeated with methyl alcohol, but at 200° C. The formation of gas was almost as rapid as before. The liquid condensed was almost neutral and contained a little aldehyde. The aluminum formed a more spongy mass containing, as before, some carbon.

The combustible gases collected over the potash contained:

Carbon monoxide	traces
Ethylene hydrocarbons	0.41
Methane	33.95
Hydrogen	65.64
	100.00

Hence the oxidation of aluminum took place principally below 200° C.

It is to be noted that the action took place in the presence of pure aluminum. Some shavings of ordinary cast aluminum having been accidentally introduced into the mixture, they were found absolutely intact and without alteration of surface which remained quite bright. This is another example of the influence of a small quantity of impurity upon the principal reaction.

The action of aluminum with formaldehyde was tried at 350° C. The slight amount of condensed liquid was acid. The gases set free were less abundant. The aluminum was only slightly attacked, but some carbon was formed.

The combustible gases collected over the potash consisted of:

Carbon monoxide	0.44
Acetylene hydrocarbons	2.19
Methane	29.03
Hydrogen	68.34
	100.00

Zinc. — Distilled zinc which would dissolve without residue in dilute acids was used. Although this metal cannot be used in engines on account of its fusibility, it serves to connect the other results obtained, for its oxide is less easily reduced than that of iron. In this respect it is intermediate between iron and aluminum.

The vapor set free at 76° C. by 95 per cent ethyl alcohol acting on the zinc at 350° C. produced much aldehyde. The condensed liquid had a specific gravity of 0.791 at 22.6° C. It was not acid. Traces of oxidation were observed, especially toward the end of the boat near the exit as if this oxidation were a secondary reaction due to the for-

mation of water or to the existence of an organic acid. No carbon was formed.

The combustible gases collected over the potash consisted of:

Carbon monoxide	0.33
Acetylene hydrocarbons	0.25
Ethylene hydrocarbons	1.43
Ethylene	5.46
Ethane	1.98
Hydrogen	90.55
	100.00

Next, vapor of 99 per cent methyl alcohol formed at a temperature of 61° C. was used. The zinc acted as before. However, there was no oxidation for the weight had not changed. Only a little aldehyde was formed, but the condensed liquid was distinctly acid and its specific gravity was 0.782 at 21.2° C.

The combustible gases collected over the potash consisted of:

Carbon monoxide	5.14
Ethylene hydrocarbons	1.15
Ethylene	0.49
Ethane	2.99
Hydrogen	90.22
	99.99

Formaldehyde vapor was passed over the zinc at 350° C. A little carbon was observed on the walls of the boat. The zinc was very slightly oxidized. The condensed liquid was very acid.

An accident prevented an analysis of the gas. It was only determined that carbon monoxide formed one per cent of the gases.

Nickel. — Pure sheet nickel was cut into filaments and put into the boat. Vapor of 95 per cent alcohol formed at 73° C. was passed over the nickel at 350° C. The nickel was changed only superficially. It became dull at the front end of the boat, but in the remaining part of the boat was unchanged, and its weight did not change. Much aldehyde was formed. The condensed liquid was scarcely acid. Its specific gravity was 0.806 at 19.8° C. No carbon was formed. Gas was produced rather abundantly.

The combustible gases collected over the potash consisted of:

Acetylene hydrocarbons	1.53
Ethylene hydrocarbons	1.63
Ethylene	7.15
Ethane	1.77
Hydrogen	87.92
	100.00

Methyl alcohol vapor was passed over the zinc at 350° C. A little carbon was deposited on the metal. Considerable aldehyde was formed. The condensed liquid was clearly acid.

The combustible gases collected over the potash consisted of:

Carbon monoxide	1.37
Ethylene hydrocarbons	0.92
Ethylene	5.02
Ethane	4.39
Hydrogen	88.30
	100.00

Formaldehyde vapor acting on the nickel at 350° C. caused no perceptible change in the weight of the metal, but there was a slight deposit of carbon. The condensed liquid was strongly acid.

The combustible gases collected over the potash consisted of:

Carbon monoxide	1.42
Acetylene hydrocarbons	5.09
Methane	26.57
Hydrogen	66.91
	99.99

Since the nickel used for valves is not pure, two experiments were made with nickel cubes broken up with a hammer. Submitted to the action of ethyl alcohol vapor at a temperature of 350° C, much aldehyde was produced. The condensed liquid was neutral and its specific gravity was 0.807 at 20° C. The metal was a little gray towards the entrance.

The combustible gases collected over the potash consisted of:

Ethylene hydrocarbons	1.36
Ethylene	5.86
Hydrogen	92.78
	100.00

The same experiment was repeated with methyl alcohol. The surface of the nickel became spongy. Little gas was formed. The specific gravity of the condensed liquid was 0.802 at 19.6° C. It contained very little aldehyde and was slightly acid.

The combustible gases collected over the potash consisted of:

Carbon monoxide	1.03
Ethylene hydrocarbons	5.69
Ethylene	4.21
Ethane	8.15
Hydrogen	80.89
	99.97

Summary. — To sum up, with only a very short contact of the gas with the metal, the decomposition of alcohol into aldehyde and hydrogen was distinctly shown. Hydrogen predominated in the combustible mixture collected.

No deposit of carbon was observed when soft iron was treated at 350° C. Zinc showed no traces of carbon and did not break up carbon monoxide. The same thing is true of pure nickel.

In almost every case ethyl alcohol yielded a mixture of ethylene and ethane that had not been observed before, and there was always a formation of acid.

Methyl alcohol yielded products less acid, sometimes neutral.

Formaldehyde when once present yielded products very acid.

With soft iron and aluminum, corrosion took place throughout the whole mass of metal. But, while with iron, whose oxides formed at low temperatures are easily reduced, there was a slow change of the wrought iron without change of weight; with aluminum, whose oxide is irreducible at the temperature used, there was a change into a powder of alumina and carbon.

In every case, and this is important from a practical point of view, the change of carbon monoxide into carbon dioxide and carbon is slower than the transformation of the alcohols into aldehyde and hydrogen. This fact should be noted in connection with the discrepancy between the author's results and those of Sabatier's experiments.

Zinc and nickel at 350° C. in the presence of the alcohols studied, suffered only a localized physical change without the formation of carbon. The change in the zinc seemed to be a secondary phenomenon, for it was ordered only at the end of the boat near the outlet. On the contrary, the nickel was changed only near the entrance of the

vapor. Hence it would seem that a state of apparent equilibrium had been produced there.

Formaldehyde yields gases similar to the preceding in which hydrogen predominates. Its decomposition is often accompanied by the formation of carbon and a large amount of acid. Hence it seems that the carbon observed by Sabatier and not by the author in the reaction of metals with the alcohols comes from a secondary reaction of the metal upon the carbon monoxide, the usual product of the decomposition of the aldehydes at the temperature used.

The presence of certain substances alloyed with the metal may greatly influence the results of the experiment. This is why in contact with gray cast iron at 350° C., the alcohols give a considerable amount of carbon. The same is true of formaldehyde. In the presence of tool steel, ethyl alcohol does not produce any carbon and methyl alcohol produces but a small amount.

Some impure aluminums are not changed.

CHAPTER XIV.

SUMMARY OF THE CHEMICAL STUDIES ON INDUSTRIAL ALCOHOL.

In the experiments carried out at temperatures distinctly below that of combustion, it has been seen that the alcohols and aldehydes are changed, either by the presence of the oxygen contained in the molecule itself, or by the presence of the air added.

Moreover, the actions are not the same in the two cases. If French denatured alcohol is used, it is advantageous to volatilize it completely in the proper amount of air before bringing it into contact with hot surfaces. Under such conditions the substance most easily altered and most dangerous as to the acid produced, namely, formaldehyde, has less chance to be formed.

Of all the substances which exist originally in the mixture, methyl alcohol ought to attract most attention. This substance begins to decompose at 160° C. into methane and formaldehyde whose disadvantages have been shown.

If the temperature is raised higher, the formaldehyde tends to disappear but another danger is encountered, which is the change of the hydrocarbons added to the alcohol into heavier and heavier products which produce tar with consequent fouling of the valves.

The same objection may be raised against acetaldehyde, but strong ethyl alcohol does not begin to decompose until about 300° C. Hence there is less chance of decomposition of the alcohol taking place in the carbureter.

If complete vaporization does not take place, small

drops of liquid may be deposited on the hot valves. More complete decompositions will then take place in the aldehydes, whether formed there or present in the original mixture. There will be produced water, carbon dioxide, and carbon monoxide. Consequently, there will be a loss of energy on account of the partial combustion before the explosion in the cylinder. Moreover, hydrocarbons are formed which have not time to diffuse uniformly through the air introduced and, consequently, give rise to incombustible mixtures such as were found in the analysis of exhaust gases.

Since methyl alcohol forms an aldehyde more easily at a low temperature than ethyl alcohol, and sets free besides a less quantity of heat per kilogram, it seems that as little of it should be used as possible. It seems to the author that the per cent required by the French government is too high.

It cannot be hoped to avoid acidity entirely, for even ethyl alcohol in the presence of oxygen at a high temperature forms a little acetic acid. This substance once formed is very difficult to burn. It is true that it remains in the state of vapor and is carried away by the exhaust as long as the engine is hot. Hence acetic acid can only be harmful while the engine is not running and if the cylinder is not greased.

It is well, moreover, to call the attention of engineers to the hydrocarbons mixed with the alcohol. Many of them contain a sulphur compound, thiophene, whose combustion forms sulphur dioxide accompanied by sulphuric acid.

The presence of an appreciable quantity of this substance may be easily determined by separating the hydrocarbon from the alcohol by the use of salt water. One tenth of its volume of strong sulphuric acid is then added to it and it

is well stirred. If at the end of ten minutes the sulphuric acid is not colored a reddish brown, the hydrocarbon is satisfactory in this regard.

The action of heat is still more complicated by the action of the ordinary metals. A comparison of the author's results with those obtained by Sabatier during a more prolonged contact shows that in the presence of the ordinary metals, wrought iron, cast iron, steel, and nickel, the alcohols commence by decomposing into aldehydes and hydrogen. Naturally, at the same time there are found the usual products of the decomposition of alcohol under the action of heat, methane, ethylene, and ethane.

If the contact is very short, as in the author's experiments, and as happens normally in good engines if there is no contact of liquid alcohol with the admission valve during the last three strokes of the engine cycle, in addition to the aldehydes already observed in the absence of the metals there will be formed as results of a secondary decomposition of the aldehydes, carbon monoxide, carbon dioxide, and the hydrocarbon homologues of acetylene, ethylene, and methane.

If the contact is prolonged, there will next result products of more advanced decomposition, especially carbon.

In the presence of metals whose oxides are easily reduced, aldehyde is burned incompletely and some acidity appears.

Moreover, a very slight change in composition of the metal causes the results to vary. For example, gray cast iron decomposes the alcohols with a deposit of carbon, while certain impure aluminums seem inert.

Lastly, some states of apparent equilibrium seem to occur so that only a small part of the metal seems to act and to be modified physically. This was observed with nickel. Apparently certain valves made of nickel owe their tarnished and pitted appearance to this fact.

Regarding the substance most commonly employed for enriching alcohol, that is, benzene, it has been shown that at 250° C. very little gas is formed in the presence of air. Hence the benzene is not appreciably changed.

At 350° C., in the presence of oxygen, even diluted, the benzene produced very finely divided carbon and is burned more decidedly than ethyl alcohol.

In the presence of metallic iron it decomposed giving a solid deposit of carbon even after a very brief contact.

Hence we are brought again to the conclusion that the liquid fuel ought to be completely vaporized in the properly calculated amount of air before reaching the very hot metallic surfaces. Under these conditions the minimum quantity of alterable organic substances will be in close contact with the hot surfaces.

It is also desirable that the area of the admission valve, and the strength of its spring when it is automatic, should be such that during the first stroke the expansion of the charge entering the cylinder will not be sufficient to condense part of the vapors in the body of the cylinder.

It is apparent that since alcohol has a greater latent heat of vaporization than petroleum, it needs special attention in this respect.

Alcohol is less inflammable than the petroleum fuels. While the mixture of alcohol vapor and air cannot burn below 17° C., air and gasoline can be lighted at − 20° C. The addition of a very small quantity of benzene is enough to cause alcohol to take fire at 0° C.

In the absence of exact experiments, it may be concluded, from the necessity of advancing the point of ignition when denatured alcohol is substituted for gasoline in any engine, that the acceleration of the reaction between air and alcohol vapor is relatively slow. This objection may be overcome by increasing the compression up to one

seventh of the initial volume and by diminishing the amount of cooling at the moment of ignition. This is accomplished as has been shown by increasing the ratio of the stroke to the diameter of the cylinder for the same compression.

After applying all these conditions, a relatively very high thermal efficiency can be expected from alcohol. At the same time a very smooth running is obtained, and except in the first explosions the disagreeable odors are avoided which are characteristic of most oil or gasoline engines.

As stated before alcohol can only be economically used in practice by means of a carbureter furnishing a constant quantity of the liquid fuel in a volume of air that contains at least 1.3 times the quantity of oxygen necessary for complete combustion. Too high a preliminary heating should be avoided. Only enough heat should be furnished to vaporize the fuel completely.

Finally, a carbureter perfectly satisfactory for a gasoline automobile engine may be absolutely useless in winter for an alcohol engine. It is better to exaggerate the conditions favorable for vaporization than to diminish them, care being taken, however, not to reach normally temperatures above 150° or 200° C.

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